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Cation-Exchange Study on a Crystalline and Thermally Stable Phase of Antimony Silicate. Effect of Irradiation on Ion-Exchange Behavior and Separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II), Ca(II), and Sr(II)

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Abstract
A systematic ion-exchange study has been performed on antimony silicate, which includes its ion-exchange capacity, elution behavior, pH titrations, and distribution coefficients of common metal ions. The $K_d$ values for alkali metals vary with the pH of the solution and the material is found to be highly selective for Rb(I) at pH values greater than 1. On the basis of distribution studies, the separation of Cd(II) from Zn(II) and Mn(II) has been achieved. Similarly, Mg(II) has been separated from Ba(II), Ca(II), and Sr(II) to illustrate its utility. Antimony silicate is very stable both thermally and chemically and possesses reproducible ion-exchange properties. Also, the effect of irradiation on the ion-exchange behavior is negligible. A tentative formula of the material has also been proposed based on chemical, infrared, and thermogravimetric analysis studies. The x-ray studies reveal that the exchanger is crystalline with a $d$-value of 6.09 Å.

INTRODUCTION
Silicates form one of the most important classes of the ion-exchange materials as they are temperature resistant and stable under chemical attack (1-4). Antimony salts such as Zr(IV), Ti(IV), and Sn(IV) antimonates (5-8) have received attention because of their reproducible ion-exchange behavior while the antimony-silicon cation exchangers have been prepared and...
studied by Novikov and co-workers (9–13). However, a systematic ion-
exchange study of antimony silicate has been lacking. Our study is
summarized in the following pages. The effect of irradiation on the ion-
exchange properties of this material is also included.

EXPERIMENTAL

Reagents

The antimony pentachloride used in this study was of ~95% purity
obtained from Koch-Light Laboratories Ltd. (Colnbrook, Bucks, England)
and the sodium silicate was a Riedal (DEHAENAG, Seelze-Hannover)
product. All other reagents and chemicals were of AnalaR grade.

Apparatus

pH measurements were made on an Elico (India) model LI-10 pH meter
while infrared studies were performed on a Beckmann IR-20 spectrophot­
ometry. X-ray studies were made on a Philips X-ray unit using a Mo-Kα
target, and the radioactivity was measured in a well-type single channel
counter of the Electronics Corporation of India Ltd. using a NaI(Tl)
detector. A Bausch and Lomb spectronic-20 colorimeter was used for the
spectrophotometric studies.

Preparation of the Reagent Solutions

A stock solution (1.0 M) of antimony pentachloride was prepared in
concentrated HCl and was diluted to the desired concentration with
demineralized water (DMW) so that the final concentration of HCl was not
less than 4 M in the solution. Sodium silicate was dissolved directly in
DMW by heating. For distribution studies, the metal salts were also
generally dissolved in DMW except the tri- and tetravalent metals for which
2–3 drops of the corresponding acids were necessary to prevent hydrolysis.

Synthesis of the Material

Different samples of antimony silicate were prepared by varying the
concentration of the mixing solutions as given in Table 1 and the pH was
fixed in the range 0–1 by adding HNO₃ with constant stirring. The gel thus
obtained was kept at room temperature (30°C) overnight, filtered, washed
TABLE 1
Preparation of Antimony Silicate (SbSi)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of each mixing solution (M) (SbCl₅ + Na-silicate)</th>
<th>Mixing ratio by volume</th>
<th>Ion exchange capacity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>0.5</td>
<td>1:1</td>
<td>Unstable in solution</td>
</tr>
<tr>
<td>S-2</td>
<td>0.4</td>
<td>1:1</td>
<td>1.6</td>
</tr>
<tr>
<td>S-3</td>
<td>0.3</td>
<td>1:1</td>
<td>1.7</td>
</tr>
<tr>
<td>S-4</td>
<td>0.2</td>
<td>1:1</td>
<td>1.5</td>
</tr>
<tr>
<td>S-5</td>
<td>0.1</td>
<td>1:1</td>
<td>1.7</td>
</tr>
<tr>
<td>S-6</td>
<td>0.1</td>
<td>2:1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

with DMW, and dried at 45°C in an air oven. It was then immersed in DMW and the granules were converted into the H⁺ form as usual (14). On the basis of its apparent chemical stability and general appearance, Sample S-6 was selected for further study. The reproducibility was checked by preparing the samples several times by the same procedure.

Composition

250 mg of the powdered exchanger was fused with ~4 g of Na₂CO₃ in a platinum crucible and transferred in a 100-mL solution of 4 M HCl. The amounts of antimony and silica in this solution were determined by standard methods (15, 16) and were found to be in the mole ratio 1:3.

Chemical Stability

250 mg of the material was placed in a 25 mL solution of an acid or a base with intermittent shaking for 24 h. The solution was then analyzed for the dissolved antimony and silica content using standard spectrophotometric methods (17, 18). The results are shown in Table 2.

Irradiation Studies

Antimony silicate (S-6) was irradiated by γ-rays obtained from a ^{60}Co source for 96 h under a dose rate of 0.4 Mrd/h using FeSO₄ as the dosimatter.
TABLE 2
Chemical Stability of SbSi

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Amount dissolved in (mg) per 25 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sb</td>
</tr>
<tr>
<td>1 M HNO₃</td>
<td>0.65</td>
</tr>
<tr>
<td>2 M HNO₃</td>
<td>2.34</td>
</tr>
<tr>
<td>4 M HNO₃</td>
<td>2.95</td>
</tr>
<tr>
<td>1 M HCl</td>
<td>1.31</td>
</tr>
<tr>
<td>2 M HCl</td>
<td>1.40</td>
</tr>
<tr>
<td>4 M HCl</td>
<td>5.11</td>
</tr>
<tr>
<td>1 M H₂SO₄</td>
<td>1.68</td>
</tr>
<tr>
<td>4 M H₂SO₄</td>
<td>3.50</td>
</tr>
<tr>
<td>2 M NaNO₃</td>
<td>0.00</td>
</tr>
<tr>
<td>4 M NaNO₃</td>
<td>0.23</td>
</tr>
<tr>
<td>2 M KNO₃</td>
<td>0.09</td>
</tr>
<tr>
<td>0.05 M NaOH</td>
<td>4.58</td>
</tr>
<tr>
<td>0.1 M NaOH</td>
<td>Dissolved</td>
</tr>
<tr>
<td></td>
<td>appreciably</td>
</tr>
<tr>
<td>0.1 M KOH</td>
<td>Dissolved</td>
</tr>
<tr>
<td></td>
<td>appreciably</td>
</tr>
<tr>
<td>0.1 M NH₄OH</td>
<td>1.68</td>
</tr>
<tr>
<td>0.5 M NH₄OH</td>
<td>4.44</td>
</tr>
</tbody>
</table>

**Ion-Exchange Capacity (i.e.c.)**

The i.e.c. was determined as usual by the column process taking 1 g exchanger (H⁺-form) in a glass tube of i.d. ~1 cm and maintaining the flow rate at ~0.5 mL/min. The total volume of the eluant necessary for the complete elution of H⁺-ions was 250 mL and the values in meq/dry g for different metals were Li(I) 1.05, Na(I) 1.60, K(I) 1.49, Mg(II) 1.53, Sr(II) 1.59, Ca(II) 1.10, Ba(II) 1.61, NH₄(I) 0.8.

**Thermal stability**

Several 1.0-g portions of Sample S-6 were heated at various temperatures in a muffle furnace for 1 h each, and the i.e.c. was determined as above by the column process after cooling them to the room temperature. The i.e.c. was also determined after heating the sample for 4 h at 400°C and 800°C.
Elution Behavior

Since the extent of elution depends upon the concentration of the eluant, a fixed volume (125 mL) of NaN0₃ solution of varying concentrations was passed through a column containing 0.5 g of the exchanger. It was observed that a 1.0 M concentration is sufficient for the complete elution of H⁺-ions from this column. The elution was therefore done with a 1.0 M solution of NaN0₃ as an eluant. Figure 1 shows the histograms of the γ-irradiated and unirradiated samples of Sb(V) silicate.

pH Titrations

These were performed by the Topp and Pepper’s method (19) by placing 500 mg of the exchanger in several 250 mL conical flasks, followed by equimolar solutions of alkali metal chlorides in different volume ratios, the final volume being 50 mL. The pH was recorded after keeping the solutions overnight for equilibrium and was plotted against the milliequivalents of the OH⁻ added. The experiment was repeated for the irradiated sample and the results are summarized in Fig. 2.

Distribution Studies

For Some Common Metal Ions

250 mg of the exchanger in the H⁺ form were shaken at 30 ± 2°C for 4 h with a 25-mL solution containing the metal ion. The initial and final concentrations of the metal ion in the solution were determined by EDTA titrations (20) as usual (21). The $K_d$ values obtained are summarized in Table 3.

For Alkali Metals

The $K_d$ values for Na(I), K(I), Rb(I), and Cs(I) were determined using radiotracers. For this purpose 100 mg of the material in the H⁺ form equilibrated with 20-mL of the solvent containing 1.0 mL of the tracer and 1.0 mL of the carrier solution of the required concentration. The initial and final metal concentrations in solution were determined by measuring the activity of the solution in the two cases. The $K_d$ values were calculated with the following formula:
Fig. 1. Histograms showing the elution behavior of antimony(V) silicate exchanger.

\[ K_d = \frac{I - F}{F} \times \frac{V}{M} \text{ mL/g} \]

where 
\( I \) = initial volume of the EDTA used or initial activity of the solution
\( F \) = final volume of the EDTA used or the final activity of the solution
\( V \) = volume of the solution
\( M \) = mass of the exchanger

The following radiotracers were used in these studies with their half-life periods shown in parentheses: \(^{24}\text{Na} (15 \text{ h}), \(^{42}\text{K} (12.5 \text{ h}), \(^{86}\text{Rb} (18.7 \text{ d}), \(^{137}\text{Cs} (30.2 \text{ years}), \(^{54}\text{Mn} (31.3 \text{ d}), \) and \(^{203}\text{Hg} (46.6 \text{ d}). \) Figure 3 shows the variation of \( K_d \) values with the pH for different alkali metals.
Separations Achieved

Several binary separations were tried using a column containing 2 g of the sized (50-100 mesh) exchanger particles taken in a glass tube having an i.d. of ~0.6 cm. The flow rate was fixed as ~0.5 mL/min using eluants selected on the basis of the $K_j$ values obtained.

RESULTS AND DISCUSSION

These studies reveal that antimony silicate is a highly stable and reproducible ion-exchange material. A comparison of its thermal stability
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Solvent</th>
<th>pH</th>
<th>DMW</th>
<th>0.01 M ClO$_4$</th>
<th>0.01 M ClO$_4$</th>
<th>10% HCl + 25% DMSO (1:20)</th>
<th>10% HCl + 25% DMSO (1:10)</th>
<th>10% HCl + 25% DMSO (1:5)</th>
<th>10% HCl + 25% DMSO (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)</td>
<td>TA</td>
<td>7</td>
<td>1800</td>
<td>36</td>
<td>159</td>
<td>30</td>
<td>19</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>TA</td>
<td>7</td>
<td>1900</td>
<td>1250</td>
<td>90</td>
<td>900</td>
<td>900</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>TA</td>
<td>7</td>
<td>433</td>
<td>14</td>
<td>28</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>TA</td>
<td>7</td>
<td>357</td>
<td>12</td>
<td>33</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>TA</td>
<td>7</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1350</td>
<td>1350</td>
<td>480</td>
<td>150</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>TA</td>
<td>7</td>
<td>1153</td>
<td>1153</td>
<td>616</td>
<td>526</td>
<td>526</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>TA</td>
<td>7</td>
<td>255</td>
<td>220</td>
<td>52</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ba(II)</td>
<td>TA</td>
<td>7</td>
<td>900</td>
<td>36</td>
<td>20</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>TA</td>
<td>7</td>
<td>866</td>
<td>45</td>
<td>32</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>TA</td>
<td>7</td>
<td>1400</td>
<td>TA</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
<td>328</td>
<td>328</td>
</tr>
<tr>
<td>VO(II)</td>
<td>TA</td>
<td>7</td>
<td>655</td>
<td>78</td>
<td>54</td>
<td>36</td>
<td>13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pt(II)</td>
<td>TA</td>
<td>7</td>
<td>175</td>
<td>633</td>
<td>214</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co(II)</td>
<td>TA</td>
<td>7</td>
<td>37</td>
<td>149</td>
<td>44</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>TA</td>
<td>7</td>
<td>1290</td>
<td>1250</td>
<td>1250</td>
<td>1250</td>
<td>1250</td>
<td>1250</td>
<td>1250</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>TA</td>
<td>7</td>
<td>600</td>
<td>1066</td>
<td>60</td>
<td>218</td>
<td>62</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>Mn(III)</td>
<td>TA</td>
<td>7</td>
<td>424</td>
<td>TA</td>
<td>424</td>
<td>1203</td>
<td>1203</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>Zn(IV)</td>
<td>TA</td>
<td>7</td>
<td>572</td>
<td>TA</td>
<td>1000</td>
<td>450</td>
<td>312</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$TA — total adsorption
with other exchangers of this class (Fig. 4) indicates a high percent retention in its i.e.c. on heating, almost comparable with the zirconium(IV) and titanium(IV) arsenophosphates prepared earlier (21). At 400°C, even heating for 4 h does not alter its i.e.c. appreciably, as seen in Table 4. This material also appears to be highly chemically stable (Table 2). The elution behavior indicates that the exchange is quite fast and almost all of the H\(^+\)-ions are eluted out in the first 50 mL of the effluent from a column of 1.0 g exchanger (Fig. 1). Moreover, the exchange takes place in one step as indicated by the pH titration curve shown in Fig. 2.

The distribution studies illustrate some of the interesting features of this material. A plot of pH versus log \(K_d\) for Na(I) and K(I) is a straight line; however, there is a positive deviation in this behavior for the Cs(I) ion above pH 5 (Fig. 3). For Rb(I), the material shows a total adsorption even above pH 1. In this respect, antimony silicate is different from Sn(IV) arsenophosphate (22) which shows a linear increase in \(K_d\) values for Rb(I) and Cs(I) with pH. Antimony silicate, therefore, appears to be specific for the Rb(I) ion and can be used for its extraction.
### Table 4

Ion Exchange Capacity and Appearance of SbSi After Heating to Various Temperatures

<table>
<thead>
<tr>
<th>Drying temperature (°C)</th>
<th>Time of heating (h)</th>
<th>Na ion exchange capacity (meq/dry g)</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1</td>
<td>1.60</td>
<td>White</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.52</td>
<td>White</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>1.42</td>
<td>Yellowish white</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>1.25</td>
<td>Yellowish white</td>
</tr>
<tr>
<td>600</td>
<td>1</td>
<td>1.20</td>
<td>Dark yellow</td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>0.72</td>
<td>Yellowish white</td>
</tr>
<tr>
<td>400</td>
<td>4</td>
<td>1.18</td>
<td>Yellowish white</td>
</tr>
<tr>
<td>800</td>
<td>4</td>
<td>0.34</td>
<td>Yellowish white</td>
</tr>
</tbody>
</table>

![Graph](image.png)

**Fig 4** Percent retention of the H⁺ ions in the exchanger phase on heating.
On the basis of its chemical composition, pH titration, and TGA results, the antimony silicate, prepared in these studies, may be tentatively assigned the following formula: \([\text{Sb}_2\text{O}_5(\text{H}_2\text{SiO}_3)_6] \cdot n\text{H}_2\text{O}\)

If it is assumed that all the exchangeable water molecules are removed on heating up to \(\sim 280^\circ\text{C}\), the first inflection point in the TGA curve (Fig. 5), the value of \(n\) can be calculated from

\[
18n = \frac{X(M + 18n)}{100}
\]

where \(X\) is the % weight loss (20%) in the exchanger on heating up to the inflection temperature and \(M\) is its molecular weight. The value of \(n\) thus obtained is 11. A further loss in weight above 280°C may be due to the
condensation process which probably continues up to 400°C, beyond which the oxides of Sb and Si are probably formed. An exhibition of the i.e.c. of SbSi even after heating to this temperature may be accounted for by the formation of antimonic acid when the oxide is dipped in aqueous solution. Antimonic acid has earlier been studied \(10, 23, 24\) as a cation exchanger.

The IR spectra show the peaks at \(\sim 450, 750, 1050, 1600,\) and \(3300\) cm\(^{-1}\) which represent \((25)\) the presence of metal hydroxides \((450\) and \(750\)\) silicates \((1050)\) and \(H_2O\) molecules \((1600\) and \(3300)\) in the structure. The x-ray studies reveal the crystalline behavior of the material with a \(d\)-value \(6.09\) Å.

An irradiation of the sample by \(\gamma\)-rays for 96 h under a dose rate of 0.4 Mrd/h does not significantly change the ion-exchange behavior and the selectivity of metal ions as indicated in Table 5. Only a slight change in the elution rate (Fig. 1) and pH titration behavior (Fig. 2) is observed on irradiation.

The utility of this material was demonstrated by achieving separations of great analytical significance: for example, Mg(II) was separated from other alkaline earths (Figs. 6 and 7). Similarly, the rather difficult separation of Cd(II) from Zn(II) was performed on this ion-exchanger with a simple eluant \(1 M\ HClO_4\) (Fig. 8). Binary separations like Cd–Mn and Hg–Pb were achieved on the columns of SbSi. Although antimonic acid has earlier shown \((10)\) a great affinity for Cd(II), it could not be utilized for its separation from Zn(II). For this purpose the SbSi exchanger prepared in these studies seems to have an added advantage. Table 6 shows the details of the six binary separations achieved on the column of this exchanger. It is clear from Table 6 that the % error observed in all cases is reasonably low and the separations can be said to be precise.

### TABLE 5

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Water (K_d ) values</th>
<th>HCIO(_4 ) (K_d ) values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Normal sample</td>
<td>Irradiated sample</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>473</td>
<td>515</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>420</td>
<td>373</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>38,394</td>
<td>36,298</td>
</tr>
</tbody>
</table>
CATION-EXCHANGE STUDY OF ANTIMONY SILICATE

Fig 6 Separation of Mg(II) from Ba(II) and Sr(II) on antimony(V) silicate columns (a) and (c). 0.1 M HClO₄, (b) and (d) 1 M HClO₄.
FIG 7 Separation of Mg(II) from Ca(II) and of Hg(II) from Pb(II) on antimony(V) silicate columns (a), 0.1 M HClO₄, (b) and (d), 1 M HClO₄, (c) 10% HCl + 5% DMSO.
FIG. 8. Separation of Cd(II) from Zn(II) and of Mn(II) on antimony(V) silicate columns: (a) and (c), 0.1 M HClO₄; (b) and (d), 1 M HClO₄.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Separations achieved (M₁ M₂)</th>
<th>Amount taken (µg)</th>
<th>Amount found (µg)</th>
<th>Error (%)</th>
<th>Eluent and its volume used for different metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn–Cd</td>
<td>200 0</td>
<td>204 0</td>
<td>0 0</td>
<td>Zn 0.1 M HClO₄, 50 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>304 0</td>
<td>309 0</td>
<td>+1.6</td>
<td>Cd 1 M HClO₄, 30 mL</td>
</tr>
<tr>
<td>2</td>
<td>Mn–Cd</td>
<td>71 0</td>
<td>67 0</td>
<td>-5.6</td>
<td>Mn 0.1 M HClO₄, 80 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>187 0</td>
<td>187 0</td>
<td>0.0</td>
<td>Cd 1 M HClO₄, 60 mL</td>
</tr>
<tr>
<td>3</td>
<td>Hg–Pb</td>
<td>240 0</td>
<td>240 0</td>
<td>0 0</td>
<td>Hg 10% HCl + 5% DMSO, 40 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>517 0</td>
<td>497 0</td>
<td>-1.8</td>
<td>Pb 1 M HClO₄, 40 mL</td>
</tr>
<tr>
<td>4</td>
<td>Mg–Ca</td>
<td>34 0</td>
<td>35 0</td>
<td>+2.6</td>
<td>Mg 0.1 M HClO₄, 70 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>64 0</td>
<td>64 0</td>
<td>0.0</td>
<td>Ca 1 M HClO₄, 50 mL</td>
</tr>
<tr>
<td>5</td>
<td>Mg–Ba</td>
<td>34 0</td>
<td>34 0</td>
<td>0 0</td>
<td>Mg 0.1 M HClO₄, 50 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>112 0</td>
<td>112 0</td>
<td>0.0</td>
<td>Ba 1 M HClO₄, 60 mL</td>
</tr>
<tr>
<td>6</td>
<td>Mg–Sr</td>
<td>48 0</td>
<td>49 0</td>
<td>+2.0</td>
<td>Mg 0.1 M HClO₄, 80 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>123 0</td>
<td>123 0</td>
<td>0.0</td>
<td>Sr 1 M HClO₄, 20 mL</td>
</tr>
</tbody>
</table>
Acknowledgments

The authors thank Prof Mohsin Qureshi for research facilities and Dr M. Sankar Das (Head, Analytical Chemistry Division, Bhabha Atomic Research Centre, Bombay) for the radiotracer facilities. The financial assistance provided by the C.S.I.R. (India) is gratefully acknowledged.

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SS-R17
Kinetics of Exchange of Alkaline Earth Metals on Antimony(V) Silicate Cation Exchanger

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Received 20 December 1982; revised and accepted 7 April 1983

A kinetic study has been performed applying the Nernst-Planck equation to the Mg\(^{2+}\) - H\(^+\), Ca\(^{2+}\) - H\(^+\), Sr\(^{2+}\) - H\(^+\) and Ba\(^{2+}\) - H\(^+\) exchange reactions on antimony(V) silicate cation exchanger at four different temperatures, viz. 25, 33, 50 and 65°C under the conditions favouring a particle diffusion controlled phenomenon only. The rate of exchange has been found to be independent of the metal ion concentration at and above the value 2 \times 10^{-2} N. The self-diffusion coefficients \(D_A\), activation energies \(E_A\) and entropies of activation \(\Delta S^*\) have also been calculated, which are useful for predicting the ion-exchange phenomenon taking place in the material.

Antimony(V) silicate has been synthesized in our laboratories as a crystalline material possessing appreciable cation-exchange capacity. Since the kinetic studies of a reaction help in understanding its mechanism, it is worthwhile to conduct such studies on the exchange process taking place on antimony(V) silicate, in view of its peculiar behaviour. The studies made so far in this direction are based on the old \(B_1\) criterion which is of limited use because of the different mobilities of the exchanging ions involved. In such cases Nernst-Planck equations should be used to obtain more precise values of the various kinetic parameters. We report here the results of such a study.

Materials and Methods

Antimony pentachloride used in this study was a Kochlight product and sodium silicate was a Riedel product. Other reagents and chemicals were BDH reagents of AR grade.

A water-bath incubator shaker having a temperature variation of \(\pm 0.5\)°C was used for the equilibrium studies.

Synthesis of antimony(V) silicate

It was synthesized by the method reported earlier.

Kinetic measurements

The rates of exchange were measured by the limited bath technique on the exchanger particles of mean radii ~ 250 \(\mu\)m (50-70 mesh size). 20 ml fractions of the metal ion solution of constant ionic strength (2 \times 10^{-2} N) were shaken with the exchanger (0.2 g) in a temperature controlled shaker at various temperatures (25, 33, 50 and 65°C) for different time intervals. The supernatant liquid was removed immediately by filtration through Whatman No.4 filter paper and the metal ions were determined in the solution with EDTA titration using Eriochrome Black-T as an indicator.

Results and Discussion

A study of the concentration effect on the rate of exchange for Mg\(^{2+}\) - H\(^+\) exchange at 33°C shows that at a concentration <2 \times 10^{-2} N, the initial rate of exchange is proportional to \(\left[\text{Mg}^{2+}\right]\). At a concentration >2 \times 10^{-2} N, it is found to be independent of the metal ion concentration. Under the conditions of particle diffusion control, a relatively large particle size of the exchanger and vigorous shaking, the fractional attainment of equilibrium is given by

\[ U(t) = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time}} \ldots (1) \]

A plot of \(U(t)\) versus \(t\) (Fig. 1) indicates that the fractional attainment of equilibrium is faster at higher temperatures, an observation analogous to that obtained for the other materials of this class. Although this is a limited bath system, the equation applicable to an infinite bath can be used here because \(CV \gg CV\) where \(C\) and \(\bar{C}\) are the metal ion concentrations in the solution and exchanger phases respectively, while \(V\) and \(\bar{V}\) are the volumes of these phases. The Nernst-Planck equations can be solved with some additional assumptions, which are valid for inorganic ion-exchangers as the swelling changes and the specific interactions are not significant in this case. As a result we obtain a coupled inter-diffusion coefficient \(D_{AB}\), the value of which depends on the relative concentrations of the counter ions A and B in the exchange phase (\(C_A\) and \(C_B\)). For \(C_A \ll C_B\) the inter-diffusion coefficient assumes the value \(D_A\), A being the counter ion initially present in the ion-exchanger phase. Since in the present study the
Thus, on the basis of the Nernst-Planck equations the numerical results can be expressed by the explicit approximation:

\[ U(t) = \left(1 - \exp\left[\pi^2 \left( f_1(a)t + f_2(a)\tau^2 + f_3(a)\tau^3\right)\right]\right)^{1/2} \quad \ldots (2) \]

where \( \tau = (D_H t)/r_0^2 \), the mobility ratio \( a = D_H/D_M \), \( r_0 \) = particle radius, and \( D_M \) is the inter-diffusion coefficient of the metal ion. The \( a \) values for the different metal ions studied are \( a_{Mg} = 6.5818 \), \( a_{Ca} = 5.8387 \), \( a_{Sr} = 5.8387 \) and \( a_{Ba} = 5.4848 \). Under the conditions \( 1 \leq a \leq 20 \) and \( Z_H/Z_M = 0.5 \), which are fulfilled in the present case, the three functions \( f_1(a) \), \( f_2(a) \) and \( f_3(a) \) can be expressed as:

\[ f_1(a) = -\frac{1}{0.64 + 0.36a^{0.668}} \quad \ldots (a) \]

\[ f_2(a) = -\frac{1}{0.96 - 2.0a^{0.4635}} \quad \ldots (b) \]

\[ f_3(a) = -\frac{1}{0.27 + 0.09a^{1.14}} \quad \ldots (c) \]

Each value of \( U(t) \) will have a corresponding value of \( \tau \) which can be obtained by solving Eq. 2 by the graphical method. The plots of \( \tau \) versus \( t \) at four different temperatures (Fig. 2) for the \( Mg^{2+} \) ion are shown at a concentration \( 2.0 \times 10^{-2} N \). The plots are linear passing through the origin thus confirming the presence of a particle diffusion controlled phenomenon. The slopes (s) of such lines for all the four alkaline earth metal ions are given in Table 1. The slopes are related with \( D_H \) (Eq. 3).

\[ s = \frac{D_H}{r_0^2} \quad \ldots (3) \]

The values of \( D_H \) obtained from Eq. (3) were plotted against \( 1/T \) (Fig. 3) when straight lines were obtained verifying the Arrhenius relation (Eq. 4).

\[ D_H = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad \ldots (4) \]

\( D_0 \) was obtained by extrapolating these curves and observing the intercept at the origin. The activation energy \( (E_a) \) was then calculated with the help of Eq. (4) taking the value of \( D_H \) as \( 273 \)°K. The entropy of activation was then calculated by using Eq. 5.

\[ D_0 = 2.72d^2 kT/h \exp\left(-\frac{\Delta S^*}{R}\right) \quad \ldots (5) \]

Table 1—Slopes of the Various \( \tau \) Versus Time Plots for Alkaline Earths

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( \tau \times 10^4 \text{s}^{-1} ) at temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})</td>
<td>8.33 10.42 14.17 18.33</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>3.61 4.17 5.00 6.25</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>3.33 5.00 5.40 6.83</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>5.21 6.25 8.17 9.44</td>
</tr>
</tbody>
</table>

![Graph](image)
### Table 2—Self-diffusion Coefficients, Energies of Activation and Entropies of Activation of Alkaline Earth Metals on Antimony(V) Silicate

<table>
<thead>
<tr>
<th>Migration ion</th>
<th>Hydrated ionic radii (Å)</th>
<th>$D_0$ (m$^2$s$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>3.10</td>
<td>6.03 x 10$^{-9}$</td>
<td>12.18</td>
<td>-53.74</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>2.00</td>
<td>6.03 x 10$^{-10}$</td>
<td>8.42</td>
<td>-72.88</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>1.80</td>
<td>8.32 x 10$^{-10}$</td>
<td>9.04</td>
<td>-70.21</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1.50</td>
<td>1.10 x 10$^{-9}$</td>
<td>9.05</td>
<td>-67.88</td>
</tr>
</tbody>
</table>

is similar to that observed earlier for tantalum arsenate and ferric antimonate.

Here $d$ is the ionic jump distance (taken as 5 Å), $k$ is the Boltzmann constant and $h$ is the Planck's constant. $T$ was taken as 273 K. The values of $D_0$, $E_a$ and $\Delta S^*$ are summarized in Table 2. The results indicate that the $E_a$ and $\Delta S^*$ values are related, to some extent, with the hydrated ionic radii of the alkaline earths. Negative $\Delta S^*$ values confirm that the behaviour of Sb(V) silicate is similar to that observed earlier for tantalum arsenate and ferric antimonate.

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### References