CHAPTER 3

KINETICS OF EXCHANGE ON SOME SYNTHETIC INORGANIC ION EXCHANGERS
Forward and Reverse Ion-Exchange Kinetics for Na\(^+\)–H\(^+\) and K\(^+\)–H\(^+\) Exchanges on Crystalline Antimony(V) Silicate

K.G. VARSHNEY, A.A. KHAN and S. RANI

Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University,
Aligarh 202002 (India)

(Received 10 September 1986, accepted in final form 8 December 1986)

ABSTRACT

The Nernst Planck equations are applied to study the ion exchange kinetics on the surface of antimony(V) silicate for the Na\(^+\)–H\(^+\) and K\(^+\)–H\(^+\) exchanges in the forward and reverse directions under conditions favouring particle diffusion. On the basis of these studies, various physical parameters such as the diffusion coefficients, activation energies and entropies of activation are evaluated.

INTRODUCTION

Antimony(V) silicate has been synthesized in these laboratories [1], showing excellent chemical stability and ion-exchange behaviour. Its utility has also been explored [1–3] in various fields including the detection of Fe(II) and Mo(VI) and the adsorption of pesticides. The kinetics of the surface phenomena occurring on these materials is also of great importance in understanding the mechanism of the ion-exchange process. Although a large number of kinetic studies on such materials have been reported [4–7], earlier approaches are based on the ‘Br’ criterion [8] which is applicable only for an isotopic exchange process [9,10]. In a true ion-exchange process where the fluxes of two different ionic species are coupled with one another [11], a single diffusion coefficient cannot describe the actual process. A new approach, based on the Nernst Planck equations [12,13] which take into account the exchange of ions having different mobilities to determine the various physical parameters, is therefore applied. The present article also deals with the reversible behaviour of antimony(V) silicate for metal–hydrogen exchanges on its surface.
EXPERIMENTAL.

Reagents and apparatus

Antimony(V) chloride and sodium silicate were products of Koch Light Laboratories Ltd (Colnbrook, Buckinghamshire, U.K.) and Riedel Dettaem A.G. (Seelze Hannover, F.R.G.), respectively. Other reagents and chemicals were of analar grade. For the equilibrium studies a waterbath incubator shaker with a temperature variation of ± 0.5°C was used. A flame photometer by Sys- tronic, India, was used for the quantitative determination of Na⁺ and K⁺.

Synthesis of antimony(V) silicate

It was synthesized as reported earlier [1]. Its ion-exchange capacities were found to be 1.6 and 1.49 meq/dry g for Na⁺ and K⁺, respectively.

Kinetic measurements

The material was finely ground and sieved in order to give particles of different mesh sizes (25-50, 52-72, 72-100 and 100-150). Particles of mean radius 121 μm (52-72 mesh) were used in the present study unless stated otherwise. Fractions (20 ml) of 0.005 N NaCl or KCl solutions were shaken with the exchanger particles (0.2 g) at various temperatures (20, 35, 50 and 65°C) for different time intervals and the supernatent liquid was analyzed for the metal ions by flame photometry. For the reverse ion exchange the material was taken in the metal form and shaken with 0.01 N HNO₃.

RESULTS AND DISCUSSION

These studies illustrate that the ion-exchange process on antimony(V) silicate is controlled by the particle diffusion at and above 0.005 N for the metal ion concentration and 0.01 N for the H⁺ concentration. The difference in concentration between the salt and acid is, perhaps, due to the difference in their ionization. Below these concentrations the film diffusion is more prominent. Under conditions of particle diffusion-controlled exchange, i.e. a relatively large particle size of the exchanger and vigorous shaking, the fractional attainment of equilibrium is given by the equation:

\[ U'(\tau) = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time}} \] (1)

A plot of \( U'(\tau) \) versus \( t \) (Fig. 1) indicates that the fractional attainment of equilibrium is faster at a higher temperature, an observation analogous to the
Fig. 1. Plots of fractional attainment of equilibrium against time for the [Na⁺ - H⁺] exchange on antimony(V) silicate at various temperatures.

earlier one [4–7]. 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 \( C' \) are the metal ion concentrations in the solution and exchanger phases, respectively, while \( V' \) and \( V \) are the volumes of these phases. Since inorganic ion exchangers do not swell significantly, the Nernst–Planck equations can be solved conveniently with some additional assumptions [11]. As a result we obtained a coupled interdiffusion coefficient \( \bar{D}_{AB} \), the value of which depends on the relative concentrations of the counter-ions ‘A’ and ‘B’ in the exchanger phase (\( \bar{C}_A \) and \( \bar{C}_B \)). For \( \bar{C}_A < \bar{C}_B \) the interdiffusion coefficient assumes the value \( \bar{D}_{AB} \) ‘A’ being the counter-ion initially present in the ion-exchanger phase.

The numerical results can be expressed [11] by the explicit approximation:

\[
U'(\tau) = \left[1 - \exp \left( \pi^2 \left( f_1(\alpha) \tau + f_2(\alpha) \tau^2 + f_3(\alpha) \tau^3 \right) \right) \right]^{\frac{1}{2}}
\]

where \( \tau \equiv D_A/r_0^2 \), mobility ratio \( \alpha \equiv \bar{D}_A/\bar{D}_M \), \( r_0 \) is the particle radius and \( \bar{D}_M \) is the interdiffusion coefficient of the metal ion. Under the conditions \( 0.1 \leq \alpha \leq 10 \) and \( Z_B/Z_M = 1 \), the charge ratio which are fulfilled in the present case, the three functions \( f_1(\alpha) \), \( f_2(\alpha) \) and \( f_3(\alpha) \) can be expressed as:

\[
f_1(\alpha) = \frac{1}{0.57 + 0.43\alpha^{0.75}}
\]

\[
f_2(\alpha) = \frac{1}{0.260 + 0.782\alpha}
\]

\[
f_3(\alpha) = \frac{1}{0.165 + 0.177\alpha}
\]

Each value of \( U'(\tau) \) will have a corresponding value of \( \tau \) which is obtained
by solving Eqn (2) by the graphical method. Plots of $\tau$ versus $t$ at the four different temperatures for $\text{Na}^+ - \text{H}^+$ (Fig. 2) and $\text{K}^+ - \text{H}^+$, and $\text{H}^+ - \text{Na}^+$ and $\text{H}^+ - \text{K}^+$ at a concentration of 0.005 $N$ and 0.01 $N$, respectively, give straight lines passing through the origin. This confirms that the phenomenon is controlled by particle diffusion. The effect of particle size on the exchange rate is given by Fig. 3 which indicates the reciprocal proportionality between the rate of exchange and the square of the particle size; this again verifies that the diffusion through exchanger particles governs the rate of exchange. Slopes ($S$) of such lines for all the four exchanges are given in Table 1 which are related to $D_A$ as follows:

![Fig. 2. Plots of $\tau$ versus time for the $[\text{Na}^+ - \text{H}^+]$ exchange on antimony(V) silicate at various temperatures.](image)

![Fig. 3. A plot of slope versus $1/r_o^2$ for the $[\text{Na}^+ - \text{H}^+]$ exchange at 35°C on antimony(V) silicate.](image)
TABLE 1

Slopes \((S)\) of plots for forward and reverse exchanges of \(\text{Na}^+ - \text{H}^+\) and \(\text{K}^+ - \text{H}^+\) on antimony (V) silicate

<table>
<thead>
<tr>
<th>Migration ion</th>
<th>Ion present at ion exchanger</th>
<th>(S \times 10^4) (s(^{-1}))</th>
<th>20°C</th>
<th>35°C</th>
<th>50°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}^+)</td>
<td>(\text{Na}^+)</td>
<td>6.11</td>
<td>12.50</td>
<td>18.33</td>
<td>32.50</td>
<td></td>
</tr>
<tr>
<td>(\text{Na}^+)</td>
<td>(\text{H}^+)</td>
<td>5.00</td>
<td>9.58</td>
<td>10.83</td>
<td>12.50</td>
<td></td>
</tr>
<tr>
<td>(\text{H}^+)</td>
<td>(\text{K}^+)</td>
<td>7.92</td>
<td>9.58</td>
<td>12.08</td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td>(\text{K}^+)</td>
<td>(\text{H}^+)</td>
<td>6.25</td>
<td>8.33</td>
<td>10.67</td>
<td>12.22</td>
<td></td>
</tr>
</tbody>
</table>

\[ S = \frac{\Delta A}{r_0^k} \]  

The values of \(\log \Delta A\) obtained by this equation are plotted against \(1/T\). Straight lines are obtained for \(\text{Na}^+\) and \(\text{K}^+\) exchanges with \(\text{H}^+\) and vice versa for reversible exchange, as shown in Fig. 4, justifying the validity of the Arrhenius equation:

\[ \Delta A = D_e \exp \left( -\frac{E_a}{RT} \right) \]

\(D_e\) was then obtained by extrapolating these curves, observing the intercept at the origin and taking the value of \(\Delta A\) at 273 K.

The entropy of activation \((\Delta S^*)\) is obtained by using Eqn (5)

\[ D_e = 2.72 d \left( \frac{kT}{h} \right) \exp \left( \frac{\Delta S^*}{R} \right) \]

where \(K\) and \(h\) are the Boltzmann and Planck constants, respectively. \(d\) is the

---

**Fig. 4.** Plots of \(-\log D_e\) versus \(1/t\) for the metal-\(\text{H}^+\) and \(\text{H}^+\)-metal exchanges on antimony (V) silicate.
TABLE 2

Self-diffusion coefficients, energies of activation and entropies of activation for forward and reverse exchanges of Na⁺ - H⁺ and K⁺ - H⁺ on antimony (V) silicate cation exchanger

<table>
<thead>
<tr>
<th>Migration ion</th>
<th>Ion present in the exchanger</th>
<th>Hydrated radius of the migration ion (Å)</th>
<th>( D_c ) (m² s⁻¹)</th>
<th>( E_a ) (kJ mol⁻¹)</th>
<th>( \Delta S^\ast ) (J K⁻¹ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Na</td>
<td>—</td>
<td>8.32 \times 10⁻⁸</td>
<td>27.6989</td>
<td>-12 7752</td>
</tr>
<tr>
<td>Na</td>
<td>H</td>
<td>2.76</td>
<td>2.88 \times 10⁻⁸</td>
<td>19.9585</td>
<td>10 7 000</td>
</tr>
<tr>
<td>H</td>
<td>K</td>
<td>—</td>
<td>2.19 \times 10⁻⁸</td>
<td>18.0302</td>
<td>-13 0161</td>
</tr>
<tr>
<td>K</td>
<td>H</td>
<td>2.32</td>
<td>3.98 \times 10⁻⁸</td>
<td>14 624</td>
<td>17 912</td>
</tr>
</tbody>
</table>

TABLE 3

Half times of exchanges for forward and reverse exchanges of Na⁺ - H⁺ and K⁺ - H⁺ on antimony (V) silicate cation exchanger

<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>Ion present in the exchanger</th>
<th>Half-time exchange, ( t_e ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20 C</td>
</tr>
<tr>
<td>H</td>
<td>Na</td>
<td>42</td>
</tr>
<tr>
<td>Na</td>
<td>H</td>
<td>66</td>
</tr>
<tr>
<td>H</td>
<td>K</td>
<td>45</td>
</tr>
<tr>
<td>K</td>
<td>H</td>
<td>45</td>
</tr>
</tbody>
</table>

ionic jump distance taken as 5 Å [14], \( R \) is the gas constant and \( T \) is taken as 273 K. As the results show, Table 2, \( D_c, E_a \) and \( \Delta S^\ast \) values decrease with the decrease in hydrated radii of Na⁺, K⁺ and H⁺. A decrease in \( \Delta S^\ast \) value also indicates a greater order of exchange. Table 3 shows that the exchange is faster at a higher temperature and that the exchanger is more selective for K⁺ ion than for Na⁺ ion. This is in accordance with an earlier observation for resins [15].

ACKNOWLEDGEMENTS

The authors are grateful to Professors A.U. Malik and K T. Nasim for providing research facilities and to the University Grants Commission (India) for financial assistance.
REFERENCES
1 KG Varshney, U Sharma, S Ram and A Premadas, Sep Sci Tech, 17 (1981-1982) 1527
3 KG Varshney, S Ram and R P Singh, Ecotoxicol Environ Saf., 10 (1985) 309
5 KG Varshney, S Agarwal and K Varshney, Colloids Surfaces, 9 (1984) 189
6 KG Varshney and S Ram, Indian J Chem., 22 (1983) 657
7 KG Varshney and S Ram, Reactive Polymers, 3 (1985) 231
12 W Z Nernst, Phys Chem., 2 (1888) 613, 4 (1889) 729
13 M Planck, Am Phys Chem., 39 (1890) 161
SHORT COMMUNICATION

ION-EXCHANGE KINETICS OF SOME DIVALENT METAL IONS ON CRYSTALLINE ANTIMONIC ACID AND ANTIMONY(V) SILICATE CATION EXCHANGERS

K G. VARSHINFY and SIMA RANI

Analytical Laboratory, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh 202001 (India)

(Received August 3 1984, accepted in revised form October 9 1984)

Knowledge of kinetics of exchange on inorganic materials is helpful for the evaluation of their separation potential. Most of the earlier studies are based on the Bt criterion [1], which is useful only for an isotopic exchange and not for a true ion exchange process [2], for which the Nernst-Planck equations are more appropriate. Since antimonic acid [3] and antimony(V) silicate [4] show promising ion exchange behaviour, we have conducted a kinetic study on the exchange of some divalent metal ions on these materials, the results of which are summarized below.

EXPERIMENTAL

Reagents and apparatus

Antimony(V) chloride and sodium silicate were the products of Koch Light Laboratories Ltd (Colnbrook Buckinghamshire, England) and Riedel (De Haen A G (Seelze, Hanover) respectively. Other reagents and chemicals were of Analar grade. For the equilibrium studies a water bath incubator shaker having a temperature variation of ±0.5°C was used.

Synthesis of materials and kinetic measurements

Antimonic acid (SbOH) was obtained [3] by the hydrolysis of antimony(V) chloride, and antimony(V) silicate (SbSi) was synthesized using our earlier method [4]. They have a Na⁺ ion exchange capacity of 1.9 and 1.6 meq/dry g, respectively. They were ground and sieved into different mesh size (25-50, 50-70, 70-100 and 100-150) particles.

For kinetic measurements, 20 ml fractions of the cation solutions of concentration 2 x 10⁻⁴ M were shaken with the exchanger particles (0.2 g) at various temperatures (25, 35, 50, or 65°C) for different time intervals, and the supernatant liquid was analyzed quantitatively for metal ions.

RESULTS

These studies illustrate that the ion exchange process on SbOH and SbSi is controlled by particle diffusion at and above a metal ion concentration of 2 x 10⁻⁴ M. Below this concentration film diffusion is more prominent. The fractional attainment of equi-
Fig. 1. Plots of fractional attainment of equilibrium versus time for Mn\(^{2+}\) on antimonite acid and antimony(V) silicate at different temperatures.

Fig. 2. Plots of fractional attainment of equilibrium versus time for Mg\(^{2+}\) on antimonite acid and antimony(V) silicate at different temperatures.
**TABLE 1**

Slopes $S$ of the various $\tau$ versus time plots for transition metals and alkaline earths on antimonial acid and antimony(V) silicate cation exchangers at different temperatures.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Particle radius ($\mu$m)</th>
<th>$S \times 10^4$ (s$^{-1}$) Antimonic acid</th>
<th></th>
<th></th>
<th>Antimony(V) silicate</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
<td>33°C</td>
<td>50°C</td>
<td>65°C</td>
<td>25°C</td>
<td>33°C</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>225</td>
<td>-</td>
<td>8.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.25</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>125</td>
<td>8.33</td>
<td>10.83</td>
<td>13.33</td>
<td>16.67</td>
<td>5.42</td>
<td>7.92</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>78.6</td>
<td>-</td>
<td>12.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.17</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>62.5</td>
<td>-</td>
<td>13.89</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.40</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>125</td>
<td>7.50</td>
<td>9.58</td>
<td>11.67</td>
<td>14.17</td>
<td>4.79</td>
<td>5.83</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>125</td>
<td>10.42</td>
<td>13.33</td>
<td>16.25</td>
<td>14.17</td>
<td>5.63</td>
<td>7.08</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>225</td>
<td>-</td>
<td>9.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.75</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>125</td>
<td>10.00</td>
<td>12.78</td>
<td>15.83</td>
<td>20.00</td>
<td>8.33</td>
<td>10.42</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>78.6</td>
<td>-</td>
<td>14.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.92</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>62.5</td>
<td>-</td>
<td>16.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14.58</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>125</td>
<td>8.89</td>
<td>10.56</td>
<td>12.22</td>
<td>14.17</td>
<td>3.60</td>
<td>4.20</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>125</td>
<td>7.08</td>
<td>7.92</td>
<td>9.17</td>
<td>11.67</td>
<td>5.33</td>
<td>5.00</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>125</td>
<td>8.33</td>
<td>10.00</td>
<td>11.67</td>
<td>13.33</td>
<td>5.20</td>
<td>6.25</td>
</tr>
</tbody>
</table>

**TABLE 2**

Self diffusion coefficient, energy of activation and entropy of activation of transition metals and alkaline earths on antimonic acid and antimony(V) silicate cation exchangers.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Antimonic acid</th>
<th></th>
<th></th>
<th>Antimony(V) silicate</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_0$ (m$^2$s$^{-1}$)</td>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>$AS^*$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>$D_0$ (m$^2$s$^{-1}$)</td>
<td>$I_a$ (kJ mol$^{-1}$)</td>
<td>$AS^*$ (J K$^{-1}$ mol$^{-1}$)</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>2.19×10$^{-9}$</td>
<td>12.55</td>
<td>-62.16</td>
<td>1.45×10$^{-9}$</td>
<td>12.34</td>
<td>-65.59</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>4.57×10$^{-10}$</td>
<td>11.15</td>
<td>-75.19</td>
<td>2.88×10$^{-10}$</td>
<td>8.94</td>
<td>-79.03</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3.98×10$^{-9}$</td>
<td>14.48</td>
<td>-57.19</td>
<td>8.71×10$^{-9}$</td>
<td>17.19</td>
<td>-50.68</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>1.95×10$^{-9}$</td>
<td>12.33</td>
<td>-63.12</td>
<td>1.58×10$^{-9}$</td>
<td>13.48</td>
<td>-64.87</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>3.16×10$^{-9}$</td>
<td>12.93</td>
<td>-59.11</td>
<td>7.59×10$^{-9}$</td>
<td>15.63</td>
<td>-51.83</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>7.24×10$^{-10}$</td>
<td>9.72</td>
<td>-71.36</td>
<td>5.13×10$^{-10}$</td>
<td>11.13</td>
<td>-74.23</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>9.33×10$^{-10}$</td>
<td>10.98</td>
<td>-69.25</td>
<td>5.50×10$^{-10}$</td>
<td>11.19</td>
<td>-73.65</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>5.50×10$^{-10}$</td>
<td>9.17</td>
<td>-73.65</td>
<td>8.32×10$^{-10}$</td>
<td>11.24</td>
<td>-70.21</td>
</tr>
</tbody>
</table>
tropy of activation are maximal for the Co\(^{2+}\)-H\(^+\) exchange and minimal for the Fe\(^{2+}\)-H\(^+\) exchange, both on SbOH and SbSi exchangers. In case of the alkaline earths these values are maximal for the Mg\(^{2+}\)-H\(^+\) exchange. However, the two materials differ when we consider the minimum values of these quantities. They are minimal for the Ba\(^{2+}\)-H\(^+\) exchange on SbOH and for the Ca\(^{2+}\)-H\(^+\) exchange on SbSi. Table 3 summarizes the half times, \(t_{1/2}\), of exchange occurring on the two ion exchangers for the metal ions studied, these half times indicate that the exchange reactions are slow.

**ACKNOWLEDGEMENT**

The Council of Scientific and Industrial Research (India) is thanked for financial assistance.

**REFERENCES**

4. K.G. Varshney, U. Sharma, S. Rani and A. Premadas, Cation-exchange study on a crystalline and thermally stable phase of antimony silicate. Effect of irradiation on ion-exchange behaviour and separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II) Ca(II) and Sr(II), Sep Sci Technol., 17 (1982/1983) 1527
3.3

A KINETIC APPROACH TO EVALUATE THE ENERGY AND ENTROPY OF ACTIVATION FOR THE EXCHANGE OF ALKALINE EARTH METAL IONS ON TIN(IV) TUNGSTATE CATION EXCHANGER

K.G. Varshney, Asif A. Khan, Kanak Varshney and Sanjay Agrawal
Analytical Laboratories,
Chemistry Section,
Faculty of Engineering & Technology,
Aligarh Muslim University,
Aligarh-202001 (INDIA).

ABSTRACT

A new approach based on the Nernst-Planck equations has been applied to study the reaction kinetics on the surface of tin(IV) tungstate for the Mg(II)-H(I), Ca(II)-H(I), Sr(II)-H(I) and Ba(II)-H(I) exchanges under the conditions favouring a particle diffusion phenomenon. On the basis of these studies the various physical parameters such as the effective diffusion coefficients, activation energies and entropies of activation have been evaluated which give some informations regarding the mechanism of ion-exchange on the surface of inorganic materials.

INTRODUCTION

Inorganic ion exchangers are well established materials for the separation of metal ions (1,2). The rate factor in the ion-exchange process is of great importance for the economic and industrial employment.
of ion exchangers. Although a large number of kinetic studies on such materials have been reported (3-9), these earlier approaches are based on the 'Bt Criterion' (10) which is applicable only for an isotopic exchange process (11,12). In a true ion-exchange process where the fluxes of two different ionic species are coupled with one another (13), a single diffusion coefficient can not describe the actual process. This article summarizes our efforts to apply the Nernst-Planck equations (14,15) which take into account the exchange of ions having different mobilities to determine the various physical parameters. Tln(IV) tungstate has been selected because it has shown high chemical stability (16) and some important analytical separations have been carried out with this exchanger (17).

EXPERIMENTAL

Reagents and Chemicals

Stannic chloride pentahydrate and sodium tungstate (B.D.H.Analar) were used. All other chemicals were of reagent grade.

Apparatus

A water-bath incubator shaker having a temperature variation of ± 0.5 °C was used in the equilibrium studies.

Synthesis, Ion-exchange Capacity and Composition of the Exchanger

Tln(IV) tungstate was synthesized by the method reported (16) earlier as follows: Aqueous solutions of 0.02M stannic chloride and 0.02M sodium tungstate were mixed in the molar ratio 2:1. The gel was digested at room temperature for several hours,
washed with water, filtered and dried at room temperature. On immersion in water it broke down to small particles with cracking and slight evolution of heat. It was converted to the hydrogen form by immersion in dil HNO₃ for 24 hr, the acid being intermittently replaced; it was then washed several times with water until the pH of the washing water was 5. Finally it was filtered and dried in air. The total ion-exchange capacity of the exchanger for Na⁺, obtained by the column process, was 0.50 meq/g which is the same as reported earlier (16). The composition was also determined by the standard methods (18-20) which confirmed the earlier results showing the molar ratio of Sn to W as 3:1.

Kinetic Measurements

Tin tungstate was ground well in order to give particles of different mesh sizes (50-70, 70-100, and 100-150). Particles of mean radii 125 μm (50-70 mesh size) were generally used unless stated otherwise. 20 ml fractions of the metal ion solutions (Mg, Ca, Sr and Ba) were shaken with 200 mg of the exchanger (H⁺ form) in several stoppered conical flasks at the desired temperatures (20, 30, 45 and 60 °C, ± 0.5 °C) for different time intervals. Supernatant liquid was immediately removed and analyzed for its metal ion content. Each run was repeated six times to evaluate the standard deviation in the results obtained.

RESULTS AND DISCUSSION

A study of the concentration effect on the rate of Mg(II)-H(I) exchange at 30 °C was made using different concentrations (0.005, 0.01, 0.02, 0.03 & 0.05M). It shows that the initial rate of exchange
is proportional to \([\text{Mg(II)}]\) up to a concentration
less than 0.03M and becomes constant at and above this
concentration. Under the conditions of particle
diffusion control (solution concentration being taken
as 0.03M), a relatively large particle size of the
exchanger and vigorous shaking, the fractional
attainment of equilibrium may be given as

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

The amount of exchange at infinite time corresponds
to the exchange at equilibrium, which is attained
after one hour of shaking as confirmed by the exchange
versus time plots. The values in meq/g (Mg, 0.50;
Ca, 0.60; Sr, 0.67; Ba, 1.2) are comparable with the
exchange capacity of the material for the metal ions
studied. The standard deviation in the determination
of \(U(\tau)\) for all the 4 metal ions was <18 x 10^{-5} \text{ (abs.)}
for six measurements. Table 1 shows the results for
Mg(II). Further calculations for the different para-
eters were made using the mean value of \(U(\tau)\) at a
particular time and temperature. Although, the
present system is a 'limited bath' the equation
applicable to an 'infinite bath' can be used here
because \(CV > \tilde{CV}\) where \(C\) and \(\tilde{C}\) are the metal ion
concentrations in the solution and the exchanger
phases, respectively, while \(V\) and \(\tilde{V}\) are the volumes of
these phases. The Kernst-Planck equations can be
solved with some additional assumptions (13) which are
valid for inorganic ion-exchangers as the swelling
changes and the specific interactions are not signi-
cificant in this case. As a result we obtain a coupled
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$U(\tau)$ (mean value of six replicates)</th>
<th>Standard deviation (abs.) $\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>30°C</td>
</tr>
<tr>
<td>1.0</td>
<td>0.58</td>
<td>0.63</td>
</tr>
<tr>
<td>1.5</td>
<td>0.69</td>
<td>0.73</td>
</tr>
<tr>
<td>2.0</td>
<td>0.77</td>
<td>0.81</td>
</tr>
<tr>
<td>2.5</td>
<td>0.83</td>
<td>0.84</td>
</tr>
<tr>
<td>3.0</td>
<td>0.88</td>
<td>0.89</td>
</tr>
</tbody>
</table>
interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter ions 'A' and 'B' in the exchanger phase ($C_A$ and $C_B$). For $C_A \ll C_B$, the interdiffusion coefficient assumes the value $\bar{D}_A$, 'A' being the counter ion initially present in the ion-exchanger phase. Since in the present study the exchanger is taken in the $H^+$-form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

Making use of the Nernst-Planck equations the numerical results can be expressed by the explicit approximation (13)

$$U(\tau) = \left\{1 - \exp \left[ \frac{D}{T} \left( f_1(\alpha)T + f_2(\alpha)T^2 + f_3(\alpha)T^3 \right) \right] \right\}^{\frac{1}{2}}$$  \hspace{1cm} (1)

where $\tau \equiv \frac{\bar{D}_H t}{r_0^2}$ and the mobility ratio is, $\alpha \equiv \frac{\bar{D}_H}{\bar{D}_N}$.

$r_0$ = particle radius and $\bar{D}_H$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 \leq \alpha \leq 20$ and $\frac{\bar{D}_H}{\bar{D}_N} = \frac{1}{2}$ which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed (13) as

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}}$$ \hspace{1cm} (a)

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}}$$ \hspace{1cm} (b)

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.14}}$$ \hspace{1cm} (c)
KINETIC APPROACH TO EVALUATE

Each value of $U(\tau)$ has a corresponding value of $\tau$ which is obtained from equation (1). Plots of $\tau$ vs. $t$ at different temperatures (Fig.1) for Mg(II) ion are shown at a concentration 0.03M, which are straight lines passing through the origin, confirming a particle diffusion controlled mechanism at this concentration. Slopes ($S$) of such lines for all the four alkaline earths are given in Table 2.

The particle size seems to have a marked effect on the exchange rate. A plot of $S$ vs. $1/r_0^2$ (Fig.2) shows the reciprocal proportionality between the rate
### Table 2: Slopes (S) of the Various \( T \) Versus Time Plots for Alkaline Earths on Tin(IV) Tungstate

<table>
<thead>
<tr>
<th>Migrating Ion</th>
<th>( S ) ( (s^{-1}) \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Mg(II) )</td>
<td>( 1.5 ) ( 1.67 ) ( 1.92 ) ( 2.17 )</td>
</tr>
<tr>
<td>( Ca(II) )</td>
<td>( 1.33 ) ( 1.50 ) ( 1.83 ) ( 2.17 )</td>
</tr>
<tr>
<td>( Sr(II) )</td>
<td>( 1.58 ) ( 1.83 ) ( 2.25 ) ( 2.67 )</td>
</tr>
<tr>
<td>( Ba(II) )</td>
<td>( 1.67 ) ( 1.92 ) ( 2.40 ) ( 3.00 )</td>
</tr>
</tbody>
</table>

**Figure 2:** Plot of \( S \) vs. \( 1/r_0^2 \) for \( Mg^{2+} \) at \( 30^\circ C \) on tin(IV) tungstate.
of exchange and square of the particle size which again verifies that the diffusion through exchanger particles is the rate governing step.

The $S$ values are related to $\bar{D}_H$ as follows:

$$S = \frac{\bar{D}_H}{r_0^2}$$  \hspace{1cm} (2)

The values of $-\log \bar{D}_H$ obtained by this equation were plotted against $1/T$. Straight lines are obtained for all the metal ions studied, as shown in Figure 3, justifying the validity of the Arrhenius equation:

$$\bar{D}_H = D_0 \exp \left( -\frac{E_a}{RT} \right)$$  \hspace{1cm} (3)

---

**FIGURE 3** Comparative plots of $-\log \bar{D}_H$ vs. $1/\text{T K}$ for $\text{Hg}^{2+}$ (O), $\text{Ca}^{2+}$ (•), $\text{Sr}^{2+}$ (Δ), and $\text{Ba}^{2+}$ (▲) on tin(IV) tungstate by the new and Bt treatments.
TABLE 3 $D_o$, $E_a$ AND $\Delta S^*$ VALUES OF ALKALINE EARTHS ON TIN(IV) TUNGSTATE IN H$^+$ FORM

<table>
<thead>
<tr>
<th>Migrating Ion</th>
<th>Ionic mobility ($m^2 v^{-1} s^{-1}$)</th>
<th>Ionic radius (nm)</th>
<th>Hydrated ionic radius (25 nm)</th>
<th>$D_o$ ($m^2 s^{-1}$)</th>
<th>$E_a$ (kJ mole$^{-1}$)</th>
<th>$\Delta S^*$ (J deg mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II)</td>
<td>5.5</td>
<td>0.078</td>
<td>0.310</td>
<td>$6.60 \times 10^{-10}$</td>
<td>8.150</td>
<td>-72.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($5.01 \times 10^{-9}$)</td>
<td>(8.880)</td>
<td>(-55.27)</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>6.2</td>
<td>0.106</td>
<td>0.200</td>
<td>$1.26 \times 10^{-9}$</td>
<td>10.03</td>
<td>-66.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($7.41 \times 10^{-9}$)</td>
<td>(11.86)</td>
<td>(-52.02)</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>6.2</td>
<td>0.127</td>
<td>0.180</td>
<td>$1.82 \times 10^{-9}$</td>
<td>10.45</td>
<td>-63.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($1.95 \times 10^{-8}$)</td>
<td>(11.92)</td>
<td>(-43.98)</td>
</tr>
<tr>
<td>Ba(II)</td>
<td>6.6</td>
<td>0.143</td>
<td>0.150</td>
<td>$3.47 \times 10^{-9}$</td>
<td>11.92</td>
<td>-58.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>($4.17 \times 10^{-8}$)</td>
<td>(13.64)</td>
<td>(-57.66)</td>
</tr>
</tbody>
</table>

The values in parantheses are those derived from the Bt Criterion.
KINETIC APPROACH TO EVALUATE

The pre-exponential constants $D_o$ are obtained from the intercepts of the lines while the $E_a$ values can be calculated from the slopes of the plots.

The entropy of activation ($\Delta S^*$) is obtained by substituting $D_o$ into the following equation:

$$D_o = 2.72 \, d^2 \, \frac{kT}{h} \exp \left( \frac{\Delta S^*}{R} \right)$$

where $k$ and $h$ are the Boltzmann and Planck constants, $d$ is the ionic jump distance taken (21) as 0.5 nm, $R$ is the gas constant and $T$ is taken as 273 K. As the results show (Table 3), $D_o$, $E_a$, and $\Delta S^*$ values increase with the ionic mobilities and radii and decrease with the hydrated ionic radii of the alkaline earths, a behaviour analogous to our earlier observations on the other inorganic ion exchangers (22-24). The values obtained of the various physical parameters explain the exchange mechanism of alkaline earths on this ion exchanger. $K_0$ values in MW observed earlier (16) on this material are in the order:

$\text{Ba(II)} > \text{Sr(II)} > \text{Ca(II)} > \text{Mg(II)}$.

The same is the order of the mobilities and activation energies as obtained in the present study.

A comparison of the different $\bar{n}_H$ values derived from the present treatment and the Bt Criterion is shown in Figure 3. The $\bar{n}_H$ values obtained by the new treatment give rise to the lower $D_o$, $E_a$, and $\Delta S^*$ values (Table 3) which suggest a more closeness to the physical processes occurring on the ion exchanger beads.
ACKNOWLEDGMENT

The authors are thankful to Prof. M. Qureshi for research facilities and to the C.S.I.R., India for the financial assistance.

REFERENCES


Received by Editor
February 13, 1984
ION-EXCHANGE KINETICS OF ALKALINE EARTH METALS ON ZIRCONIUM(IV) ARSENOPOPHOSPHATE: LINEAR VARIATION OF ENERGY AND ENTROPY OF ACTIVATION WITH IONIC RADII AND MOBILITY

KRISHNA GOPAL VARSHNEY, SANJAY AGRAWAL and KANAK VARSHNEY
Analytical Laboratories, Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202001 (India)
(Received 23 July 1984; accepted in final form 17 October 1984)

ABSTRACT

The kinetics of Mg(II), Ca(II), Sr(II) and Ba(II) exchange with H(I) on zirconium(IV) arsenophosphate cation exchanger was studied applying the Nernst—Planck equations. The rate of exchange is found to be particle diffusion controlled at a metal ion concentration > 0.01 M in aqueous medium. The energy and entropy of activation vary linearly with the ionic radii and mobilities.

INTRODUCTION

Zirconium-based ion exchangers have received attention because of their excellent ion-exchange behaviour and some important chemical applications [1]. Zirconium(IV) phospho- and silico-arsenates prepared earlier in these laboratories have shown a good selectivity for metal ions and reproducibility in ion-exchange behaviour [2, 3]. A kinetic study has also been performed on these materials for the exchange of some transition metals applying the Nernst—Planck equations [4]. Their practical utility has been explored in the detection and separation of metal ions [5, 6] and in the analysis of some real samples, such as rocks and pharmaceuticals, which are rich in alkaline earth metals [7—10]. The following pages summarise the results of our kinetic study to understand the mechanism of exchange of alkaline earth metal ions on zirconium(IV) arsenophosphate cation exchanger.

MATERIALS AND METHODS

Reagents and chemicals

Zirconyl chloride, trisodium orthophosphate and disodium arsenate used in this study were obtained either from BDH (Poole, U.K.) or Merck (Darmstadt, F.R.G.). All other reagents and chemicals were of AnalaR grade.
Apparatus

A waterbath incubator shaker with a temperature variation of ± 0.5°C was used for the equilibrium studies.

Synthesis of the ion exchanger

Zirconium(IV) arsenophosphate was synthesised by the method described earlier [11]. Its modified phase, obtained by heating at 200°C for 1 h [2], has shown an improvement in its ion-exchange characteristics and chemical stability and was therefore used for the present studies.

Kinetic measurements

The ion exchanger was carefully ground in order to obtain it in different mesh sizes (40—60, 70—100, 100—150, 170—200) and the kinetic measurements were made at 20, 30, 45 and 60°C by the procedure reported earlier [4].

RESULTS AND DISCUSSION

Under the conditions favouring a particle diffusion and at infinite solution volume [12], the fractional attainment of equilibrium, $U(r)$, can be expressed by the relation

$$U(r) = \left(1 - \exp\left[\pi^2 \left(f_1(\alpha)r + f_2(\alpha)r^2 + f_3(\alpha)r^3\right)\right]\right)^{1/5} \quad (1)$$

where $r$ is $D_{H}/r_0^2$; mobility ratio, $\alpha = D_{H}/D_{M}$; $r_0$ is the particle radius; and $D_{M}$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 < \alpha < 20$ and the charge ratio, $Z_{H}/Z_{M} = 1/2$, which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as:

$$f_1(\alpha) = \frac{1}{0.64 + 0.36 \alpha^{0.666}}$$

$$f_2(\alpha) = \frac{1}{0.96 - 2.0 \alpha^{0.4635}}$$

$$f_3(\alpha) = \frac{1}{0.27 + 0.09 \alpha^{1.14}}$$

A solution of Eqn (1) for each value of $U(r)$ gives a corresponding value of $\tau$. A study of the $\tau$ versus $t$ plots for different metal-ion concentrations (0.005, 0.008, 0.01 and 0.025 M) at 30°C indicates that they are straight lines passing through the origin at a concentration $\geq 0.01$ M (Fig. 1), suggesting a particle diffusion controlled exchange. It is further confirmed by the...
Fig. 1. Plots of $r$ versus $t$ for Mg(II)–H(I) exchange using different solution concentrations at 30°C: 0.005 M (•); 0.008 M (○); 0.01 M (○); 0.025 M (★).

TABLE 1

Slopes ($S$) of $T$ versus $t$ plots for the alkaline earth metal ions on zirconium(IV) arsenophosphate ($r_a = 150 \mu m$)

<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>$S \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>2.08</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>2.08</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>2.42</td>
</tr>
<tr>
<td>Ba(II)</td>
<td>2.80</td>
</tr>
</tbody>
</table>

inverse variation of the slopes ($S$) of these straight lines with the square of the particle radii. The $S$ values as summarised in Table 1 are related to $D_H$ as follows

$$S = \frac{D_H}{r_a^2}$$  \hspace{1cm} (2)

$-\log D_H$ values thus obtained vary linearly with $1/T$ (Fig. 2), verifying the Arrhenius equation

$$D_H = D_0 \exp \left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (3)
The slopes of these straight lines give the energies of activation \( (E_a) \), and the intercepts with the Y-axis give the \( D_0 \) values, which are related to the entropy of activation \( (\Delta S^*) \) as 

\[
D_0 = 2.72 \, d^2 \, h \, T / h \exp (\Delta S^* / R)
\]

where \( h \) and \( h \) are the Boltzmann and Planck constants, respectively; \( d \) is the ionic jump distance \([13]\) taken as 5 Å; \( R \) is the gas constant; and \( T \) is taken as 273 K. Table 2 summarises the values of \( D_0, E_a \) and \( \Delta S^* \). An increase in the values of \( E_a \) and \( \Delta S^* \) with the ionic radii and mobilities \([14]\) of alkaline earth metals is a general behaviour of the inorganic ion exchangers. Figure 3 shows a linear variation of \( E_a \) and \( \Delta S^* \) with ionic radii, hydrated ionic radii and ionic mobilities. Zirconium(IV) arsenosilicate also shows such behaviour \([15]\). It is in contrast with our earlier observation for transition metals on these materials \([4]\).

\[
\text{TABLE 2}
\]

\begin{tabular}{|l|c|c|c|c|c|}
\hline
Metal ion & Ionic mobility & Ionic radius & Hydrated ionic radius & \( D_0 \) & \( E_a \) & \( \Delta S^* \) \\
exchanging with & \( \text{(cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}) \) & \( \text{(Å)} \) & \( \text{(Å)} \) & \( \text{(m}^2 \, \text{s}^{-1}) \) & \( \text{(kJ mol}^{-1} \) & \( \text{(J deg}^{-1} \, \text{mol}^{-1}) \) \\
H\(^+\) & & & & & & \\
\hline
Mg(II) & 0.00055 & 0.78 & 3.10 & \( 2.0 \times 10^{-8} \) & 14.74 & -43.79 \\
Ca(II) & 0.00062 & 1.06 & 2.00 & \( 9.5 \times 10^{-8} \) & 18.40 & -30.77 \\
Sr(II) & 0.00062 & 1.27 & 1.80 & \( 1.7 \times 10^{-7} \) & 19.65 & -25.79 \\
Ba(II) & 0.00066 & 1.43 & 1.50 & \( 3.5 \times 10^{-7} \) & 21.11 & -20.05 \\
\hline
\end{tabular}

\*Goldschmidt's value.
Fig. 3. Variation of $E_a$ and $\Delta S^*$ with ionic radii, hydrated ionic radii and ionic mobilities of alkaline earth metals on zirconium(IV) arsenophosphate.

A comparison of the kinetic behaviour of various inorganic ion exchangers as shown in Fig. 4 indicates that the diffusion rate, activation energy and entropy of activation are, in general, lower on single salts [16–18] than on double salts [15, 19]. A positive entropy change on zirconium(IV) arsenosilicate probably accounts for the high efficiency of its columns [3].

ACKNOWLEDGEMENTS

The authors thank Professor M. Quereshi for research facilities. The financial assistance provided by the C.S.I.R., India, is gratefully acknowledged.
REFERENCES

7 K G Varshney, S Agrawal and K Varshney, J Liq Chromatogr, 6 (1983) 1535
8 K G Varshney, S Agrawal, K Varshney, A Premadas, MS Rathi and PP Khanna, Talanta, 30 (1983) 955
Kinetics of Ag\(^+\), Cu\(^+\), Mg\(^+\), Ca\(^+\), Sr\(^+\), Ba\(^+\) & Y\(^+\) Exchange in Sn(IV) Arsenophosphate

K. G. Varshe1 & A. Premadas

Chemistry Section, Z. H. College of Engineering & Technology, Aligarh Muslim University, Aligarh 202 001

Received 21 October 1980; revised and accepted 12 January 1981

The kinetics of exchange reactions of Ag\(^+\), Cu\(^+\), Mg\(^+\), Ca\(^+\), Sr\(^+\), Ba\(^+\) and Y\(^+\) ions on Sn(IV) arsenophosphate have been studied at 23\(^\circ\), 30\(^\circ\), 40\(^\circ\) and 60\(^\circ\) under the conditions favoring the particle diffusion mechanism only. At a concentration 0.1 \(N\), rate of exchange has been found to be independent of the metal ion concentration. The diffusion coefficients, activation energies and entropies of activation have also been calculated.

\[ F = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time}} \]

Now, in the present case \(CV \gg CV\) where \(C\) is the concentration of metal ion in the solution phase, \(V\) is the volume of the solution, \(C\) is the concentration of the metal ion in the exchanger phase, and \(V\) is the volume of the exchanger. Thus, although the system is, in principle, a limited bath, the equation applicable to the infinite bath can be used in this case also as also verified by Reichenberg \(^{16}\), Helfferich \(^{17}\) and Blickenstaff \(^{18,19}\) in their studies.

Hence, \(F = 1 - \frac{6}{n^2} \sum_{n=1}^{\alpha} \frac{1}{n^2} \exp(-n^2 \text{ } Bt) \) \ldots(1)
where \( B = \frac{r^2}{r^3} D_i \) \( \ldots (2) \)

\( r \) = radius of the particle and \( D_i \) = the effective diffusion coefficient of the two ions undergoing exchange within the exchanger. Values of \( Bt \) as a function of \( T \) may be calculated as given by Reichenberg. The \( Bt \) versus \( t \) plots, at four selected temperatures, are shown in Fig. 1, for \( Cu^{2+} \) ion (C. 0.1 N). Similar curves are obtained for \( Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} \) and \( Y^{3+} \). At higher temperatures, the rate of exchange is faster and attains the equilibrium more quickly. The \( B \) values calculated from these plots are given in Table 1.

**Table 1 — B Value as a Function of Temperature and Particle Size**

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>( B ) Value</th>
<th>( 23°C )</th>
<th>( 30°C )</th>
<th>( 40°C )</th>
<th>( 60°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(^+)</td>
<td>99.7</td>
<td>1.51x10^{-3}</td>
<td>1.62x10^{-3}</td>
<td>1.97x10^{-3}</td>
<td>2.45x10^{-3}</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>99.7</td>
<td>7.41x10^{-4}</td>
<td>8.48x10^{-4}</td>
<td>9.37x10^{-4}</td>
<td>1.22x10^{-3}</td>
</tr>
<tr>
<td>Cu(^{3+})</td>
<td>61.0</td>
<td>9.03x10^{-3}</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cu(^{4+})</td>
<td>41.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cu(^{5+})</td>
<td>34.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>99.7</td>
<td>8.30x10^{-4}</td>
<td>8.70x10^{-4}</td>
<td>9.03x10^{-4}</td>
<td>1.10x10^{-3}</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>99.7</td>
<td>8.40x10^{-4}</td>
<td>9.03x10^{-4}</td>
<td>9.60x10^{-4}</td>
<td>1.23x10^{-3}</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>99.7</td>
<td>9.80x10^{-4}</td>
<td>1.12x10^{-3}</td>
<td>1.25x10^{-3}</td>
<td>1.51x10^{-4}</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>97.7</td>
<td>1.02x10^{-4}</td>
<td>1.25x10^{-4}</td>
<td>1.43x10^{-4}</td>
<td>1.70x10^{-4}</td>
</tr>
<tr>
<td>Y(^{3+})</td>
<td>99.7</td>
<td>6.02x10^{-4}</td>
<td>6.34x10^{-4}</td>
<td>7.21x10^{-4}</td>
<td>8.33x10^{-4}</td>
</tr>
</tbody>
</table>

\( r \) mean radius of the particle.

*Fig. 1 — Influence of temperature on the rate of exchange for \( Cu^{2+} \) using \( Sn(IV) \) arsenophosphate (H\(^+\)). [1, 23°C; 2, 30°C; 3, 40°C; 4, 60°C]*

The effect of the particle size upon the rate of exchange was studied for the exchange of \( Cu^{2+} \) ion upon the exchanger particle of different mean radii (Fig. 2). The results show that the exchange rate increases with the decrease in the particle size which is in agreement with the fundamental condition of the particle diffusion.

Equation (2) was used for the calculation of diffusion coefficient (\( D_i \)). A plot of log \( D_i \) versus \( 1/T \) is a straight line for all the metal ions used, as shown in Fig. 3. The values of \( E_a \) (energy of activation) were obtained by applying the Arrhenius equation \( D_i = D_o \exp \left( -E_a / RT \right) \). As Table 2 suggests, \( E_a \) increases with a decrease in the hydrated radii for alkaline earths. This behaviour is similar to that of the monovalent cations migrating through analcite. We may conclude therefore that the hydrated ionic radii contribute to the mechanism of exchange reaction in two ways: (a) by affecting the position of equilibrium, and (b) by affecting the rate of attainment of equilibrium. It indicates the feasibility of separating ions by exploiting difference in their rate of exchange on \( Sn(IV) \) arsenophosphate.

\( D_o \) is related with the entropy of activation (\( \Delta S^* \)) as follows,

\( D_o = 2.72 \ d^2 \ kT / h \exp \left( \Delta S^*/R \right) \) \( \ldots (3) \)

where \( d \) is the ionic jump distance taken as 5 \( \AA \), \( k \) is the Boltzmann constant and \( h \) is the Planck's constant, \( T \) is taken as 303 K. Table 2 summarizes the calculated values of \( \Delta S^* \) which are negative as observed in tantalum arsenate and ferric antimonate also. A comparison of \( \Delta S^* \) values for alkaline earths reveals that it increases with increasing ionic radii. The same conclusion was drawn by Freeman and Staimers in \( Y \)-zeolite.
<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>Hydrated ionic radii (Å)</th>
<th>$D_o$ (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>Ag$^+$</td>
<td>3.0</td>
<td>1.11 x 10$^{-4}$</td>
<td>10.63</td>
<td>-68.68</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>2.0</td>
<td>5.11 x 10$^{-16}$</td>
<td>10.30</td>
<td>-75.13</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>3.10</td>
<td>1.49 x 10$^{-18}$</td>
<td>7.14</td>
<td>-85.38</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>2.00</td>
<td>2.02 x 10$^{-18}$</td>
<td>7.82</td>
<td>-82.85</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>1.80</td>
<td>4.56 x 10$^{-18}$</td>
<td>9.32</td>
<td>-76.08</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1.50</td>
<td>1.40 x 10$^{-18}$</td>
<td>11.88</td>
<td>-66.75</td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>1.25 x 10$^{-18}$</td>
<td></td>
<td>7.49</td>
<td>-86.83</td>
</tr>
</tbody>
</table>

The authors are thankful to Prof. M. Qureshi and Prof. W. Rahman for research facilities and to the CSIR, New Delhi for financial assistance to one of them (A. Premadas).

References
3.6 EVALUATION OF THE ENERGY AND ENTROPY OF ACTIVATION FOR THE FORWARD AND REVERSE EXCHANGES OF ALKALINE EARTH METALS ON ANTIMONY(V) ARSENOPHOSPHATE CATION EXCHANGERS-A KINETIC APPROACH

K.G. Varshney, A.A. Khan and Ashfaq Rabbani Khan
Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002, India

Received December 14, 1988
Accepted April 24, 1989

Forward and reverse ion exchange kinetics have been studied on antimony(V) arsenophosphate for the Ba(II)-H⁺, Ca(II)-H⁺, Sr(II)-H⁺ and Mg(II)-H⁺ exchanges under conditions favoring a particle diffusion. On the basis of these studies various physical parameters have been evaluated, such as the diffusion coefficients, activation energies and entropies of activation.

INTRODUCTION

Energy and entropy of activation play a vital role in understanding the reactions occurring in a system. Recently, we have studied these parameters only for the forward processes.
VARSHNEY et al.: ENERGY OF ACTIVATION

[1-4] on the basis of the Nernst-Planck equations [5,6] as against the old Bt criterion [7-11] proposed by Boyd et al. [12]. No studies have been made so far for the forward and reverse exchanges on inorganic ion-exchangers for alkaline earths. Only the Na\(^+\)-H\(^+\) and K\(^+\)-H\(^+\) exchanges have been studied earlier in these labs on antimony(V) silicate [13]. In order to extend such studies further the present work was undertaken, the results of which are summarized in the following pages. The matrix selected has been the antimony(V) arsenophosphate exchanger and the metal ions taken are the alkaline earths.

EXPERIMENTAL

All chemicals and reagents were of Analar grade. A water-bath incubator shaker having a temperature variation of ±0.5 °C was used in the equilibrium studies.

Synthesis of the Ion Exchange Material. Antimony(V) arsenophosphate was prepared as earlier [14].

Kinetic Measurements. Ion exchanger particles of mean radii 121 μm (50-72 mesh size) in H\(^+\) form were used in this experiment. 20 ml fractions of the 0.05 M metal ion solution (Mg, Ca, Sr and Ba) were shaken with 200 mg of the exchanger in several stoppered conical flasks at the desired temperature (20, 30, 45 and 60 ±0.5 °C) for different time intervals. Determination of supernatant liquid were done by EDTA titrations. In the reverse process the exchanger was taken in the metal form and shaken with 20 ml of 0.1 M HNO\(_3\). The supernatant liquid was titrated against a standard NaOH solution to find out the amount of the H\(^+\) ions adsorbed on the exchanger.

RESULTS AND DISCUSSION

Kinetic measurements were performed on the surface of antimony(V) arsenophosphate under conditions favoring a particle diffusion-controlled ion exchange for forward and reverse exchanges of Mg(II)-H\(^+\), Ca(II)-H\(^+\), Sr(II)-H\(^+\) and Ba(II)-H\(^+\). The fractional attainment of equilibrium \(U_{(t)}\) may be expressed as:
Each value of $U(t)$ has a corresponding value of $\tau$ (a dimensionless time parameter) obtained from our previous work [15] by substituting the various values in the following equation [16]:

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

Plots of $\tau$ vs. $t$ at the four different temperatures for metal(II)-H$^+$ and H$^+$-metal(II) exchanges at a concentration of 0.05 M (metal) and 0.1 M (hydrogen) are shown in Fig. 1. Straight lines passing through the origin confirm the particle diffusion phenomenon.

Slopes (S) of such lines for all the forward and reverse exchanges are given in Table 1 which are related to $\tilde{D}_A$ as follows:

$$S = \frac{\tilde{D}_A}{T_0}$$

Table 1

<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>Ion present in the ion exchanger</th>
<th>20 °C $S$ (s$^{-1}$)</th>
<th>30 °C $S$ (s$^{-1}$)</th>
<th>45 °C $S$ (s$^{-1}$)</th>
<th>60 °C $S$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II) H$^+$</td>
<td>1.5x10$^{-2}$</td>
<td>1.9x10$^{-2}$</td>
<td>2.9x10$^{-2}$</td>
<td>4.5x10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>H$^+$ Mg(II)</td>
<td>1.75x10$^{-2}$</td>
<td>3.0x10$^{-2}$</td>
<td>3.87x10$^{-2}$</td>
<td>5.0x10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Ca(II) H$^+$</td>
<td>1.0x10$^{-2}$</td>
<td>1.5x10$^{-2}$</td>
<td>1.9x10$^{-2}$</td>
<td>2.5x10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>H$^+$ Ca(II)</td>
<td>1.0x10$^{-2}$</td>
<td>1.62x10$^{-2}$</td>
<td>2.25x10$^{-2}$</td>
<td>2.87x10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Sr(II) H$^+$</td>
<td>0.85x10$^{-2}$</td>
<td>1.05x10$^{-2}$</td>
<td>1.35x10$^{-2}$</td>
<td>1.9x10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>H$^+$ Sr(II)</td>
<td>1.40x10$^{-2}$</td>
<td>2.20x10$^{-2}$</td>
<td>3.8x10$^{-2}$</td>
<td>5.0x10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Ba(II) H$^+$</td>
<td>0.35x10$^{-2}$</td>
<td>0.55x10$^{-2}$</td>
<td>0.80x10$^{-2}$</td>
<td>1.15x10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>H$^+$ Ba(II)</td>
<td>1.4x10$^{-2}$</td>
<td>1.8x10$^{-2}$</td>
<td>2.7x10$^{-2}$</td>
<td>3.8x10$^{-2}$</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. Plots of $\tau$ versus time for Mg(II)-$H^+$ and $H^+$-Mg(II) exchange on antimony(V) arsenophosphate at different temperatures.

The value of $\log \delta_A$ obtained by this equation are plotted.
against $\frac{1}{T}$, for forward and reverse exchanges shown justifying the validity of the Arrhenius equation

$$D_A = D_0 \exp \left( -\frac{E_a}{RT} \right)$$

The pre-exponential constants, $D_0$, are obtained by extrapolating these curves observing the intercept at the Y axis, and taking the value of $D_A$ at 273 K.

The energy of activation ($E_a$) values can be calculated by the use of the above equation. While the entropy of activation ($\Delta S^*$) is obtained by using the following equation

$$D_0 = 2.72 d^2 \frac{kT}{h} \exp \left( -\frac{\Delta S^*}{R} \right)$$

where $k$ and $h$ are the Boltzman and Planck constants, respectively, $d$ is the ionic jump distance taken [17] as 0.5 nm; $R$ is the gas constant and $T$ is taken as 273 K. The values of $D_0$, $E_a$ and $\Delta S^*$ are summarized in Table 2. As the results show, the

<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>Ionic mobility radii</th>
<th>Hydrated ionic radii</th>
<th>$D_0$</th>
<th>$E_a$</th>
<th>$\Delta S^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($10^2 \text{m}^2\text{V}^{-1}\text{s}^{-1}$)</td>
<td>($\text{Å}$)</td>
<td>($\text{Å}$)</td>
<td>($\text{kJ mol}^{-1}$)</td>
<td>($\text{J} \text{K}^{-1} \text{mol}^{-1}$)</td>
</tr>
<tr>
<td>Mg(II) H⁺</td>
<td>5.5 0.78 3.1</td>
<td>8.41 x 10⁻⁷</td>
<td>19.85</td>
<td>-12.69</td>
<td></td>
</tr>
<tr>
<td>H⁺ Mg(II)</td>
<td>- - -</td>
<td>5.6 x 10⁻⁶</td>
<td>23.64</td>
<td>+3.06</td>
<td></td>
</tr>
<tr>
<td>Ca(II) H⁺</td>
<td>6.2 1.06 2.0</td>
<td>7.07 x 10⁻⁷</td>
<td>20.24</td>
<td>-14.13</td>
<td></td>
</tr>
<tr>
<td>H⁺ Ca(II)</td>
<td>- - -</td>
<td>4.73 x 10⁻⁶</td>
<td>24.82</td>
<td>+1.66</td>
<td></td>
</tr>
<tr>
<td>Sr(II) H⁺</td>
<td>6.2 1.27 1.8</td>
<td>5.01 x 10⁻⁷</td>
<td>24.95</td>
<td>-16.99</td>
<td></td>
</tr>
<tr>
<td>H⁺ Sr(II)</td>
<td>- - -</td>
<td>7.90 x 10⁻⁶</td>
<td>25.34</td>
<td>+5.93</td>
<td></td>
</tr>
<tr>
<td>Ba(II) H⁺</td>
<td>6.6 1.43 1.5</td>
<td>17.78 x 10⁻⁷</td>
<td>25.08</td>
<td>-6.46</td>
<td></td>
</tr>
<tr>
<td>H⁺ Ba(II)</td>
<td>- - -</td>
<td>3.16 x 10⁻⁶</td>
<td>22.86</td>
<td>-1.68</td>
<td></td>
</tr>
</tbody>
</table>
negative values of $\Delta S^*$ indicate that the ion exchange process is more feasible on antimony(V) arsenophosphate when the exchanger phase is in $H^+$ form and exchanged by a metal ion. For a forward exchange, there is a decrease in the $\Delta S^*$ values with the decrease in the hydrated radii except for the $H^+-Ba(II)$ ex-

Fig. 2. Diffusion coefficients, activation energies and entropies of activation for alkaline earth metals exchanging with $H^+$ on different inorganic ion exchangers
change showing a greater exchange in that order. For the reverse exchange, however, the trend is not certain.

A comparison of kinetic behavior of various inorganic ion exchangers in Fig. 2 indicates higher values of $\Delta S^*$ and $E_a$ for antimony (V) arsenophosphate as compared to other materials of this class.

Acknowledgements. The authors thank Professor K.T. Nasim for research facilities. The financial assistance provided by the C.S.I.R., India is gratefully acknowledged.

REFERENCES

5. W.Z. Nernst: Phys.Chem., 2, 613 (1888); 4, 729 (1889)
K. G. Varshney* and U. Sharma

(Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology,
Aligarh Muslim University, Aligarh-202002, India)

Received April 2, 1983
In revised form June 17, 1983
Accepted for publication July 13, 1983

Kinetics of the exchange reactions of Mn^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+} ions on Zr(IV) and Th(IV) phosphosilicate cation exchangers has been studied at 25, 32, 50 and 65 °C under the conditions favourable to the particle diffusion mechanism only and the rate of exchange has been found to be independent of the metal ion concentration at and above 0.01 M in aqueous medium on both the materials. Various kinetic parameters such as self-diffusion coefficient (D), energy of activation (ΔE) and entropy of activation (ΔS*) have been calculated which are useful for predicting the ion exchange phenomenon taking place.

Introduction

Inorganic ion exchangers are generally used for the metal separations. They are superior to the organic resins as they are resistant to heat and radiation. To understand the mechanism underlying in an ion exchange process its kinetic studies are essential which have been done mostly on the crystalline and amorphous zirconium phosphate [1—5], zirconium oxide [6], tantalum and tin arsenates [7, 8], ceric phosphate [9] and zirconium, iron and tin antimonates [10—12]. Moreover, these studies are based on the old Bt criterion [13] which is not very useful for an ion exchange process because of the different effective diffusion coefficients taking part in such a case. Here, the Nernst—Planck [14, 15] equations are more appropriate. Since the kinetic studies are rarely made [16—18] on double salts, the following pages summarize our study on zirconium(IV) and thorium(IV) phosphosilicates (ZPS and TPS) as cation exchangers, taking transition metal ions as exchanging species with H^+ ions.

Experimental

Reagents and chemicals

Zirconyl chloride and thorium nitrate were of B.D.H. (England) while sodium silicate was a Riedel (DEHAENAG, Seelze Hannover) product. All other reagents and chemicals were of AnalaR grade.

* To whom correspondence should be addressed
Apparatus

A water bath incubator shaker having a temperature variation of ± 0.5 °C was used for the equilibrium studies.

Synthesis of the ion exchange materials

To a definite volume of a 0.1 M sodium silicate (Na₂SiO₃ • 3H₂O) solution conc. HCl (5 ml per 100 ml Na-silicate solution) and a definite volume of a 0.1 M zirconium oxychloride (ZrOCl₂ • 8H₂O) solution were added. The pH of the mixture was made 9 ± 10 by adding NH₄OH and the resultant slurry was allowed to stand overnight. It was filtered, washed with DMW and mixed with a fixed volume of a HNO₃ — H₂O mixture (1 M in terms of each acid). The gel thus obtained was kept overnight, filtered out, washed thoroughly with DMW, dried at 15 °C in an air oven and was craked in DMW to form small granules. The granules were then placed in 1 M HNO₃ to convert them into the H⁺-form and were finally washed and dried at 45 °C before use for further study. TPS was prepared in a similar manner by taking thorium nitrate Th(NO₃)₄ • 6H₂O instead of zirconium oxychloride. The Na⁺ ion exchange capacities of these materials (ZPS and TPS) were found to be 2.19 and 1.66 meq/dry g, respectively.

Kinetic measurements

The rates of exchange of metal ions were determined by the limited bath technique. 20 mL fractions of the 0.01 M metal ion solutions of the divalent transition metals (Mn²⁺, Fe²⁺, Co²⁺ and Ni²⁺) were shaken with 200 mg of the exchanger beads (mean radius 120 μm; 100 — 150 mesh size) in some stoppered conical flasks at the desired temperature (25, 32, 50 and 65 °C ± 0.5 °C) for different time intervals as mentioned in Fig. 2. Supernatant liquid was immediately removed by filtering through a Whatman No. 1 filter paper and the determinations were done by EDTA titrations [19] using Eriochrome Black T as an indicator.

Results and Discussion

A study of the concentration effect on the rate of Mn⁺ — H⁺ exchange at 25 °C shows that at concentrations < 0.01 M the initial rate of exchange is proportional to [Mn²⁺]. At concentrations ≥ 0.01 M it is found to be independent of the metal ion concentration. Under the conditions of a particle diffusion control, a relatively large particle size of the exchanger and vigorous shaking the fractional attainment of equilibrium may be given as,

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

A plot of \( U(t) \) versus \( t \) (Fig. 1) for Mn²⁺ ion on ZPS and TPS indicates that the fractional attainment of equilibrium is faster at a higher temperature, an observation analogous to 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 \( CV \gg \bar{C} \bar{V} \) where \( C \) and \( \bar{C} \) are the metal ion concentrations in the solution and exchanger phases, respectively. \( V \) and \( \bar{V} \) are the volumes of these two phases. The Nernst—Planck equations can be solved with some additional assumptions [20], 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 interdiffusion coefficient $D_{\lambda 1}$, the value of which depends on the relative concentrations of the counter ions $A$ and $B$ in the exchanger phase ($C_A$ and $C_B$). For $C_A \ll C_B$ the interdiffusion coefficient assumes the values $D_{\lambda A}$, $A$ being the counter ion initially present in the ion exchanger phase. Since in the present case the exchanger is taken in $H^+$ form, $D_{\lambda A}$ may be replaced by $D_{\lambda H}$.

Thus, on the basis of the Nernst—Planck equations

$$U(\tau) = 1 - \exp \left\{ \left[ \frac{\tau^2}{D_{\lambda H}} f_1(\chi) \tau^2 + f_2(\chi) \tau^2 + f_3(\chi) \tau^2 \right] \right\}$$

(2)

where

$$\tau = \frac{D_{\lambda H} t}{r_0^2}$$

and the mobility ratio $\alpha = \frac{D_{\lambda H}}{D_{\lambda M}}$, $r_0$ particle radius and $D_{\lambda M}$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 < \alpha < 20$ and $Z_{\lambda H}Z_M = 1/2$ as in the present case, the three functions $f_1(\chi)$, $f_2(\chi)$ and $f_3(\chi)$ can be expressed [21] as:

$$f_1(\chi) = \frac{1}{0.64 + 0.36 \chi^{0.458}}$$

(a)

$$f_2(\chi) = \frac{1}{0.96 - 2.0 \chi^{0.485}}$$

(b)

and

$$f_3(\chi) = \frac{1}{0.27 + 0.09 \chi^{1.44}}$$

(c)
Each value of $U(r)$ will have a corresponding value of $\tau$ which is obtained on solving equation (2) by graphical method. The plots of $\tau$ vs. $t$ at the four different temperatures (Fig. 2) on ZPS and TPS for the Mn$^{2+}$ ions are shown at a concentration 0.1 M which are straight lines passing through the origin. It confirms a particle diffusion controlled phenomenon. The slopes ($S$) of such lines for all the four transition metals on ZPS and TPS are given in Table I, which are related with $\bar{D}_H$ as follows:

$$S = \frac{\bar{D}_H}{r_0^2}$$

(3)

The plots of $-\log \bar{D}_H$ vs. $1/T$ are straight lines as shown in Fig. 3, thus verifying the Arrhenius relation:

$$\bar{D}_H = D_0 e^{(E_a/RT)}$$

(4)

![Fig. 2](image)

![Fig. 3](image)
Table I

Slopes of the various τ versus time plots for transition metals on Zs(IV) and Th(IV) phosphosilicates

<table>
<thead>
<tr>
<th>Ion</th>
<th>25 °C</th>
<th>35 °C</th>
<th>55 °C</th>
<th>65 °C</th>
<th>25 °C</th>
<th>35 °C</th>
<th>55 °C</th>
<th>65 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>1.27 × 10⁻¹⁴</td>
<td>1.55 × 10⁻¹⁴</td>
<td>1.77 × 10⁻¹⁴</td>
<td>2.44 × 10⁻¹⁴</td>
<td>1.83 × 10⁻¹⁴</td>
<td>3.16 × 10⁻¹⁴</td>
<td>4.16 × 10⁻¹⁴</td>
<td>5.33 × 10⁻¹⁴</td>
</tr>
<tr>
<td>Fe⁺⁺</td>
<td>6.38 × 10⁻¹⁴</td>
<td>7.77 × 10⁻¹⁴</td>
<td>1.11 × 10⁻¹⁴</td>
<td>1.44 × 10⁻¹⁴</td>
<td>1.00 × 10⁻¹⁵</td>
<td>1.33 × 10⁻¹⁵</td>
<td>2.16 × 10⁻¹⁵</td>
<td>2.66 × 10⁻¹⁵</td>
</tr>
<tr>
<td>Co⁺⁺</td>
<td>1.00 × 10⁻¹⁴</td>
<td>1.27 × 10⁻¹⁴</td>
<td>1.72 × 10⁻¹⁴</td>
<td>3.11 × 10⁻¹⁴</td>
<td>3.33 × 10⁻¹⁴</td>
<td>5.00 × 10⁻¹⁴</td>
<td>9.44 × 10⁻¹⁴</td>
<td>16.11 × 10⁻¹⁴</td>
</tr>
<tr>
<td>Ni⁺⁺</td>
<td>1.11 × 10⁻¹⁴</td>
<td>1.33 × 10⁻¹⁴</td>
<td>1.72 × 10⁻¹⁴</td>
<td>3.33 × 10⁻¹⁴</td>
<td>1.66 × 10⁻¹⁴</td>
<td>2.33 × 10⁻¹⁴</td>
<td>3.16 × 10⁻¹⁴</td>
<td>4.00 × 10⁻¹⁴</td>
</tr>
</tbody>
</table>
Table II
Self-diffusion coefficient, energy of activation and entropy of activation of transition metals on Zr(IV) and Th(IV) phosphosilicates

<table>
<thead>
<tr>
<th>Transition ion</th>
<th>Ionic mobility (m^2 volt^{-1} s^{-1})</th>
<th>Ionic radii (nm)</th>
<th>$D_0$, $E_a$ and $\Delta S^\circ$ values</th>
<th>$D_0$, $E_a$ and $\Delta S^\circ$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_0$ (m^2 s^{-1})</td>
<td>$E_a$ (kJ mol^{-1})</td>
<td>$\Delta S^\circ$ (J K^{-1} mol^{-1})</td>
<td>$D_0$ (m^2 s^{-1})</td>
</tr>
<tr>
<td>Mn^{2+}</td>
<td>$55 \times 10^{-9}$</td>
<td>$9.1 \times 10^{-1}$</td>
<td>$3.55 \times 10^{-10}$</td>
<td>$13.07$</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>$54 \times 10^{-9}$</td>
<td>$6.7 \times 10^{-1}$</td>
<td>$8.41 \times 10^{-9}$</td>
<td>$16.85$</td>
</tr>
<tr>
<td>Co^{2+}</td>
<td>$55 \times 10^{-9}$</td>
<td>$8.2 \times 10^{-1}$</td>
<td>$1.88 \times 10^{-8}$</td>
<td>$23.52$</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>$52 \times 10^{-9}$</td>
<td>$7.8 \times 10^{-1}$</td>
<td>$1.99 \times 10^{-8}$</td>
<td>$23.25$</td>
</tr>
</tbody>
</table>
$D_0$ is then obtained by extrapolating these lines and observing the intercepts at the origin. $E_a$ values are then calculated from equation (4) putting the value of $D_H$ corresponding to the $T$ value as 273 °K in the graph. Finally $\Delta S^*$ values are obtained from the expression:

$$D_0 = 2.72 \sigma d^2 \frac{kT}{h} \exp (\Delta S^*/R)$$

(5)

where $d$ is the ionic jump distance [22] taken as 0.5 nm and $k$ and $h$ are the Boltzmann and Planck constants, respectively. $T$ is taken as 273 °K. The values of $D_0$, $E_a$ and $\Delta S^*$ are summarized in Table II.

The authors are thankful to Prof. Mohsin Qureshi for the research facilities and to the C.S.I.R., India for the financial assistance.

REFERENCES

ION-EXCHANGE KINETICS OF SOME METAL POLLUTANTS AND THEIR SEPARATION ON ZIRCONIUM(IV) PHOSPHO- AND SILICO-ARSENATE CATION EXCHANGERS

KRISHNA GOPAL VARSHNEY, SANJAY AGRAWAL and KANAK VARSHNEY
Analytical Laboratories, Chemistry Section, Z.H. College of Engineering & Technology, Aligarh Muslim University, Aligarh 202 001 (India)
(Received 29 July 1983; accepted in final form 4 October 1983)

ABSTRACT

Exchange kinetics of some polluting metal ions such as Mn(II), Fe(II), Co(II), Ni(II), Zn(II) and Cd(II) has been studied on zirconium(IV) phospho- and silico-arsenates, applying an approach based on the Nernst—Planck equations. As a result, some kinetic and thermodynamic parameters like diffusion coefficients, activation energies, and entropies of activation have been evaluated under the conditions favouring a particle diffusion-controlled mechanism. The theoretical predictions derived from these studies have been correlated with the practically achieved separations of cadmium(II) from some metals mentioned above.

INTRODUCTION

Zirconium(IV) phospho- and silico-arsenates have been synthesized in these laboratories [1, 2] showing excellent chemical stability and ion-exchange behaviour. They are highly selective for the heavy metals like iron, manganese, cobalt, nickel, cadmium, lead, zinc and copper, which are hazardous to health when adsorbed by the body beyond certain limits. Their utility has also been explored [2—6] in various fields including the analysis of rocks, alloys and drugs and water purification. Kinetic study of the ion exchange process occurring on the surface of such materials is important for their economic and industrial employment. We have earlier made such a study on some inorganic ion exchangers [7—10] applying a new approach based on the Nernst—Planck equations [11, 12] replacing the old “Bt criterion” [13—20], which is useful only for the ions having similar effective diffusion coefficients, i.e. for an isotopic exchange. In an ion-exchange process the fluxes of two different ionic species are coupled with one another [21] and, therefore, a single diffusion coefficient cannot describe the actual process. In the present paper, we have made an effort to understand the mechanism of the metal uptake by the phospho- and silico-arsenates of zirconium(IV) in aqueous media containing some heavy metal pollutants and to correlate the theoretical predictions with the practically achieved separations.

0166-6622/84/$03.00 © 1984 Elsevier Science Publishers B.V.
MATERIALS AND METHODS

Reagents and chemicals

Zirconyl chloride, trisodium orthophosphate, disodium arsenate and arsenic acid used in this study were obtained either from the B.D.H., Poole (U.K.) or E. Merck (Darmstadt, F.R.G.). Sodium silicate was a Riedel (DEHAENAG, Seele Hannover, F.R.G.) product and all other reagents and chemicals were of AnalaR grade.

Apparatus

A waterbath incubator shaker having a temperature variation of ± 0.5°C was used for the equilibrium studies.

Synthesis of the ion-exchange materials

Zirconium(IV) arsenophosphate (ZAP) and zirconium(IV) arsenosilicate (ZAS) were synthesized by the methods reported earlier [1, 2] which involve the precipitation of the materials, filtration through a vacuum pump, drying at a particular temperature (40—45°C), cracking in demineralized water (DMW) and then converting into the H+-form by treatment with a dilute HNO₃ solution. Before being used for further studies, ZAP was heated at 200°C for 1 h in a muffle furnace to get a modified phase (α-ZAP) of this material which has shown improved ion-exchange behaviour and chemical stability [3]. The reported values of the Na⁺ ion-exchange capacities of ZAS and α-ZAP are 1.30 and 1.03 meq/dry g, respectively.

Kinetic measurements

The materials were finely carefully ground in order to give particles of different mesh sizes (40 —60, 50 —70, 70 —100 and 100—150). Particles of mean radii 125 μm (of ZAS) and 150 μm (of α-ZAP) were generally used in the present study unless stated otherwise. Fractions (20 ml) of the metal ion solutions were shaken with 250 mg of the exchanger (H⁺-form) in several stoppered conical flasks at the desired temperatures (20, 30, 45 and 60°C) for different time intervals. The supernatant liquid was removed immediately and the determinations were done as usual by EDTA titrations [22]. Each set was repeated six times and the mean values were taken for further calculations.

Separation procedure

Two grams of the 40 —60 mesh sized particles of the exchanger (α-ZAP) in H⁺-form were used for the column operation in a glass tube having an in-
ternal diameter of 0.6 cm. The column was washed thoroughly with DMW
and the mixture to be separated was loaded on it, maintaining a flow rate of
ca. 0.1 ml/min. The elution of the metal ion other than Cd(II) was done by
0.01 M HNO₃, selected on the basis of Kₐ values [3]. Cd(II) was removed
finally with 1 M HNO₃. The flow rate for eluting the metal ions was kept to
c. 0.4 ml/min. Cd(II) was also quantitatively recovered from a synthetic
mixture containing Mn(II), 137.5 µg; Co(II), 147.3 µg; Ni(II), 146.8 µg;
Zn(II), 162.5 µg and Cd (II), 280 µg, using the same eluants as described
above.

RESULTS AND DISCUSSION

A high metal ion concentration, relatively large particle size of the ex-
changer and vigorous shaking are the basic conditions for a particle diffu-
sion-controlled ion-exchange phenomenon. Under these conditions the
fractional attainment of equilibrium, U(τ) may be expressed as

\[ U(τ) = \frac{\text{the amount of exchange at time } τ}{\text{the amount of exchange at infinite time (equilibrium)}}. \]

The present system may be considered to follow the "infinite solution
volume" condition [23] because CV > CV, where C and C are the metal-ion
concentrations in the solution and exchanger phases respectively, and V and
\( \bar{V} \) are the volumes of these phases. The Nernst—Planck equations can be
solved with some additional assumptions [24] which are valid for an in-
organic ion-exchanger as the swelling changes and the specific interactions
are not significant in this case. As a result, we obtain a coupled interdiffusion
coefficient \( D_{AB} \), the value of which depends on the relative concentrations
of the countereions A and B in the exchanger phase (\( C_A \) and \( C_B \)). For
\( C_A = C_B \), the interdiffusion coefficient assumes the value \( D_A \), A being the
counter ion initially present in the ion-exchanger phase. Since in the present
study the exchanger is taken in the H⁺-form, \( D_A \) may be replaced by \( D_H \).

The numerical results can be expressed [25] by the explicit approximation:

\[ U(τ) = \left(1 - \exp\left[\frac{2}{r^2} f_1(α) r + f_2(α) r^2 + f_3(α) r^3\right]\right)^{\frac{1}{2}} \]

where \( r = D_H / r_0^2 \)

mobility ratio, \( α = D_H / D_M \), \( r_0 = \text{particle radius and } D_M \) is the interdiffusion
coefficient of the metal ion. Under the condition \( 1 < α < 20 \) and the charge
ratio, \( Z_H / Z_M = 1/2 \) which are fulfilled in the present case, the three func-
tions \( f_1(α) \), \( f_2(α) \) and \( f_3(α) \) can be expressed [26] as:

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

\[ f_2(α) = -\frac{1}{0.96 - 2.0α^{0.4635}} \]

(b)
Each value of $U_\tau$ will have a corresponding value of $\tau$ which is obtained on solving Eq. (1) by the graphical method. The concentration effect on the mechanism of exchange was studied at $30^\circ C$ by taking different metal ion concentrations ($0.005, 0.008, 0.01, 0.025, 0.05, 0.1$ and $0.12 \text{ M}$). The plots of $\tau$ vs. $t$ (Fig. 1) at the metal ion concentrations $> 0.1 \text{ M}$ for ZAS and $> 0.01 \text{ M}$ for $\alpha$-ZAP, are straight lines passing through the origin, thus confirming a particle diffusion-controlled exchange at these concentrations. The slopes ($S$) of the $\tau$ vs. $t$ plots, as shown for the Mn$^{2+}$$-\text{H}^+$ (Fig. 2) exchange, are summarized in Table 1 for all the metal ions studied at the concentration $0.1 \text{ M}$ for ZAS and $0.01 \text{ M}$ for $\alpha$-ZAP.

The particle size has a marked effect on the rate of exchange. A plot of $S$ vs. $1/r^2$ (Fig. 3) shows that the rate of exchange is inversely proportional to the particle size, a fundamental condition for a particle diffusion phenomenon.

The $S$ values are related with $\bar{D}_H$ as follows:

$$S = \frac{\bar{D}_H}{r^2}$$

(2)

The log $\bar{D}_H$ is related linearly with $1/T$ (Figs. 4, 5) in all cases, justifying the validity of the Arrhenius equation:

$$\bar{D}_H = D_0 \exp \left(-\frac{E_a}{RT}\right)$$

(3)

The preexponential constants ($D_0$) were obtained from the intercepts of these lines and the values of activation energy ($E_a$) were calculated from Eq. (3). The entropies of activation ($\Delta S^*$) were obtained by substituting the $D_0$ va-
Fig. 2. Plots of $r$ vs. $t$ for Mn$^{3+}$-H$^+$ exchange at different temperatures on ZAS and a-ZAP under the conditions of particle diffusion.

TABLE 1

Slopes ($S$) of $r$ vs. $t$ plots for the transition metals on ZAS and a-ZAP

<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>$S$ ($s^{-1} \times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>ZAS</td>
<td>a-ZAP</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>1.43 1.83</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>1.93 1.77</td>
</tr>
<tr>
<td>Co(II)</td>
<td>1.68 2.07</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>1.84 1.94</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>1.60 0.72</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>1.33 1.16</td>
</tr>
</tbody>
</table>

ues in the equation:

$$D_0 = 2.72d^2kT/h \exp(\Delta S^*/R)$$  \hspace{1cm} (4)

where $k$ and $h$ are the Boltzmann and Planck constants, respectively; $d$ is the ionic jump distance [27] as taken 5 Å, $R = 8.3144 \text{ J deg}^{-1} \text{ mol}^{-1}$ is the gas constant and $T$ is taken as 273°K. Table 2 summarizes the $D_0$, $E_a$ and $\Delta S^*$ values on ZAS and a-ZAP.

As table 2 indicates, the $\Delta S^*$ values are negative on both the ion exchangers, an observation analogous to most of the materials of this class [13–16, 18–20]. It also indicates that the activation energies for the various transition metal ions studied do not have a definite trend as far as their varia-
Fig. 3. Plots of $S$ vs. $1/r^2$ for Mn$^{2+}$ at 30°C on ZAS and α-ZAP.

Fig. 4. Plots of $-\log D_H$ vs. $1/T$K for Fe$^{3+}$ (○); Co$^{2+}$ (●); Ni$^{2+}$ (○); Mn$^{2+}$ (●); Zn$^{2+}$ (●) and Cd$^{2+}$ (x) on ZAS.
TABLE 2

\( D_e, E_a \) and \( \Delta S^* \) values for the \( H^+ \)-exchange with transition metal ions on ZAS and \( \alpha \)-ZAP

<table>
<thead>
<tr>
<th>Metal ion exchanging with ( H^+ )</th>
<th>Ionic radius (( \text{\AA}^* ))</th>
<th>( D_e ) (m(^3) s(^{-1}))</th>
<th>( E_a ) (kJ mole(^{-1}))</th>
<th>( \Delta S^* ) (J deg(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(II)</td>
<td>0.91</td>
<td>( 3.55 \times 10^{-4} )</td>
<td>12.26</td>
<td>-58.15</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.83</td>
<td>( 2.95 \times 10^{-4} )</td>
<td>16.62</td>
<td>-40.53</td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.82</td>
<td>( 1.74 \times 10^{-4} )</td>
<td>8.482</td>
<td>-44.94</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.78</td>
<td>( 7.76 \times 10^{-5} )</td>
<td>13.69</td>
<td>-51.64</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.83</td>
<td>( 7.41 \times 10^{-5} )</td>
<td>19.52</td>
<td>-32.88</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>1.03</td>
<td>( 2.04 \times 10^{-5} )</td>
<td>22.42</td>
<td>-24.45</td>
</tr>
</tbody>
</table>

Fig. 5. Plots of \( -\log D_H \) vs. \( 1/T^0 \)K for Fe\(^{3+} \) (○); Co\(^{3+} \) (●); Ni(II) (○); Mn(II) (●); Zn(II) (●) and Cd(II) (●) on \( \alpha \)-ZAP.

With the ionic radii is concerned. It is in contrast to the observation made earlier [7, 8] on these materials for the alkaline earths. It may be due to a more distinct variation in the ionic radii in a particular group than in a
period. The activation energy is maximum for Cd(II) on both the exchangers. However, the variation in its value for the different metal ions is much wider on α-ZAP as compared to the one on ZAS. These observations are supplemented by the achieved separations of Cd(II) from Co(II), Ni(II), Mn(II) and Zn(II) on α-ZAP columns as shown in Fig. 6. The achievement of the Cd(II)—Zn(II) separation appears to be unusual on the basis of our kinetic observations. They are separated although their $E_a$ values are similar, which depend upon the mobility ratios ($\bar{D}_M/\bar{D}_M$). However, the separation tenden-

Fig. 6. Elution curves for the separation of Cd(II) from other metal ions on α-ZAP columns.
cy of the two metals depends on their ionic sizes also, which are very different in this case. This may be the reason for the unusual behaviour of the material (α-ZAP) for this particular separation. Thus, these studies, based on the Nernst—Planck equations, give a more appropriate explanation for the separation mechanism on inorganic ion-exchangers as compared to the old Bt criterion because of the introduction of the term "mobility" in the new approach.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Mohsin Qureshi for research facilities. The financial assistance provided by the C.S.I.R., India, is gratefully acknowledged.

REFERENCES

23 Ref. 21, p. 260.
24 Ref. 21, p. 268.
25 Ref. 21, p. 270.
26 Ref. 21, p. 271.
ION EXCHANGE KINETICS OF ALKALINE
EARTHS ON Zr(IV) ARSENOSILICATE
CATION EXCHANGER

ACTIVATION ENERGY AS A LINEAR FUNCTION
OF THE IONIC MOBILITIES AND RADIi

K. G. VARSHNEY*, S. AGRAWAL and K. VARSHNEY
(Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology,
Aligarh Muslim University, Aligarh-202001, India)

Received May 17, 1983
Accepted for publication June 28, 1983

A new approach based on the Nernst–Planck equations has been applied to study
the ion exchange kinetics for the exchange reactions of Mg(II), Ca(II), Sr(II) and
Ba(II) with H+ ions at various temperatures on the zirconium(IV) arsenosilicate phase.
Under the conditions of particle diffusion, the rate of exchange was found to be inde­
pendent of the metal ion concentration at and above 0.1 M in aqueous medium. Energy
and entropy of activation were determined and found to vary linearly with the ionic
radii and mobilities of alkaline earths, a unique feature observed for an inorganic ion
exchanger. The results are useful for predicting the ion exchange processes occurring
on the surface of an inorganic material of the type studied.

Introduction

Inorganic ion exchangers are useful for the separation of metals [1,2].
Although a large number of such materials have been prepared, only a few
of them have been reported for their kinetic studies [3—21]. Moreover, the
earlier approaches are based on the old 'Bt criterion' [22] which is useful only
for ions having similar effective diffusion coefficients i.e. for the isotope
exchange processes. In an ion exchange phenomenon, however, the fluxes of
two different ionic species are coupled into one another [23], and, therefore,
a single diffusion coefficient can not describe the actual process. This article,
therefore, summarizes our efforts to apply the Nernst–Planck equations
[24, 25] which take into account the exchange of ions having different mobili­
ties to determine the various kinetic parameters. Zirconium(IV) arsinosilicate
(ZAS) has been selected because of its fairly good stability, reproducibility
and applicability in the analysis of some real samples [26, 27].
Experimental

Reagents and chemicals

Zirconyl chloride and arsenic acid used in this study were BDH (England) products while sodium silicate was the product of Riedel (DEHAENAG, Selze Hannover). Other reagents and chemicals were of ananalytical grade.

Apparatus

A water-bath incubator shaker having a temperature variation of ±0.5 °C was used in the equilibrium studies.

Synthesis of the ion exchange material

ZAS was prepared as earlier [26] by the following method: An aqueous (0.1 M) sodium silicate solution, made acidic (pH 0–1) by adding HCl, was mixed with an aqueous (0.1 M) zirconyl chloride solution and the pH of the mixture was raised to 8–10 by a slow addition of ammonium hydroxide with intermittent shaking to obtain a slurry. After filtration and washing with demineralized water (DMW), it was treated with a 1:1 (V/V) mixture of 0.5 M solutions of arsenic and nitric acids. This resulted in a gel which was digested at room temperature for 24 h and then separated by filtration. It was washed thoroughly to remove excess acid, dried at 45 °C and cracked into small granules by putting in DMW and then converted into the H⁺-form using 1 M HNO₃. They were finally washed with DMW and dried as usual for further study. The Na⁺-exchange capacity of the material was found to be 1.3 meq/dry g as determined by the column process.

Kinetic measurements

Ion exchange particles of mean radii 250 μm (55–65 mesh size) were used in this experiment. 20 ml fractions of the 0.1 M metal ion solution (Mg, Ca, Sr and Ba) were shaken with 200 mg of the exchanger in several stoppered conical flasks at the desired temperature (20, 30, 45 and 60 °C, ±0.5 °C) for different time intervals. Supernatant liquid was immediately removed by filtering it through a Whatman No. 4 filter paper. Determinations were done by EDTA titrations [26] using Erichrome Black T as an indicator. Each run was repeated at least six times.

Results and Discussion

A study of the concentration effect on the rate of exchange for Mg²⁺—H⁺ exchange at 30 °C shows that at concentrations <0.1 M the initial rate of exchange is proportional to [Mg(II)]. At concentrations ≥0.1 M 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 may be given as

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

A plot of \( U(t) \) versus \( t \) (Fig. 1) indicates that the fractional attainment of equilibrium is faster at a higher temperature, an observation analogous to 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 \( CV \gg C \bar{V} \) where \( C \) and \( \bar{C} \) are the metal ion concentrations in the solution and the 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 [23] 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 interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter ions 'A' and 'B' in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$, the interdiffusion coefficient assumes the value $\bar{D}_A$, 'A' being the counter ion initially present in the ion exchanger phase. Since in the present study the exchanger is taken in the $H^+$ form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

Thus, on the basis of the Nernst—Planck equations the numerical results can be expressed by the explicit approximation [25]

$$U(\tau) = \left(1 - \exp \left(\tau^2 (f_1(\alpha) \tau + f_2(\alpha) \tau^2 + f_3(\alpha) \tau^3)\right)^\frac{1}{4}\right)$$

(1)

where $\tau = \frac{\bar{D}_H t}{r_0^2}$, mobility ratio $\alpha = \frac{\bar{D}_H}{\bar{D}_M}$, $r_0$ = particle radius and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 \leq \alpha \leq 20$ and $\frac{Z_{H^+}}{Z_M} = \frac{1}{2}$ which are fulfilled in the present case, the three functions $f_1(\alpha), f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36e^{\alpha}}$$
Each value of $U(\tau)$ will have a corresponding value of $\tau$ which is obtained by solving the equation (1) by graphical method. Plots of $\tau$ vs. $t$ at the four different temperatures (Fig. 2) for Mg(II) ion are shown at a concentration 0.1 M which are straight lines passing through the origin. This confirms that the phenomenon is particle-diffusion controlled. Table I Slopes ($S$) of such lines for all the four alkaline earths are given in Table 1 which are related with $D_{II}$ as follows;

$$S = \frac{\bar{D}_{II}}{t_0^{S(t)}}$$  \hspace{1cm} (2)

### Table 1

<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>$S(t)$ at 20°C</th>
<th>$S(t)$ at 30°C</th>
<th>$S(t)$ at 45°C</th>
<th>$S(t)$ at 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II)</td>
<td>$1.50 \times 10^{-3}$</td>
<td>$2.56 \times 10^{-3}$</td>
<td>$4.42 \times 10^{-3}$</td>
<td>$9.26 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>$1.75 \times 10^{-3}$</td>
<td>$2.78 \times 10^{-3}$</td>
<td>$4.90 \times 10^{-3}$</td>
<td>$11.10 \times 10^{-3}$</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>$1.34 \times 10^{-3}$</td>
<td>$2.08 \times 10^{-3}$</td>
<td>$4.35 \times 10^{-3}$</td>
<td>$7.90 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ba(II)</td>
<td>$1.08 \times 10^{-3}$</td>
<td>$1.79 \times 10^{-3}$</td>
<td>$3.55 \times 10^{-3}$</td>
<td>$7.20 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The values of log $D_H$ obtained by this equation were plotted against $1/T$. Straight lines are obtained for all the metal ions studied, as shown in Fig. 3, justifying the validity of the Arrhenius equation;

$$D_H = D_0 \exp \left( \frac{-E_a}{RT} \right)$$

(3)

The pre-exponential constants $D_0$ are obtained from the intercepts of the lines and then the $E_a$ values can be calculated by the use of this equation.

The entropy of activation ($\Delta S^*$) is obtained by substituting $D_0$ into the following equation

$$D_0 = 2.72 d^2 \frac{kT}{h} \exp \left( \frac{-\Delta S^*}{R} \right)$$

(4)

where $k$ and $h$ are the Boltzmann and Planck’s constants, $d$ is the ionic jump distance taken [29] as 0.5 nm, $R$ is the gas constant and $T$ is taken as 273 $^\circ$K.

The values of $D_0$, $E_a$ and $\Delta S^*$ are summarized in Table II. As the results show $E_a$ increases with the ionic radii as usual. Positive entropy changes may be due to the deformation in the shape of the matrix because of the introduction

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{Migrating ion} & \textbf{Ionic mobility} & \textbf{Ionic radii} & \textbf{Hydrated ionic radii} & \textbf{$D_0$ $m^2 \cdot s^{-1} \cdot s^{-1}$} & \textbf{$E_a$ kJ mol$^{-1}$} & \textbf{$\Delta S^*$ J K$^{-1}$ mol$^{-1}$} \\
\hline
Mg(II) & 5.5 & 0.078 & 0.310 & $1.36 \times 10^{-4}$ & 34.53 & 29.57 \\
Ca(II) & 6.2 & 0.106 & 0.200 & $2.93 \times 10^{-4}$ & 36.05 & 35.98 \\
Sr(II) & 6.2 & 0.127 & 0.180 & $3.85 \times 10^{-4}$ & 37.55 & 38.25 \\
Ba(II) & 6.6 & 0.143 & 0.150 & $4.47 \times 10^{-4}$ & 38.28 & 39.49 \\
\hline
\end{tabular}
\caption{Energy of activation and entropy of activation of alkaline earths on ZAS in H$^+$-form}
\end{table}
of larger ions in place of the previously present $H^+$ ions in the matrix. A similar behaviour has also been observed earlier for the exchange of Co(III) amine complex cations on chromium ferrocyanide gel [17]. We found linear relations between $E_a$ and $\Delta S^*$ values and the ion mobilities and radii of the alkaline earths as shown in Fig. 4.

The authors are thankful to Prof. Mohsin Qureshi for research facilities and to the CSIR (India) for financial assistance.

REFERENCES


3.10 Kinetics of Exchange of Some Divalent Metal Ions on Phosphosilicates of Zirconium(IV) & Thorium(IV) & Arsenosilicate of Tin(IV)

K. G. Varshney*, U. M. Sharma, S. Anwar & A. A. Khan

Chemistry Section, Faculty of Engg & Tech., Aligarh Muslim University, Aligarh 202002
Received 21 March 1983; revised 30 September 1983; accepted 17 October 1983

Kinetics of the exchange reactions of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions on Zr(IV) and Th(IV) phosphosilicates and Sn(IV) arsenosilicate cation exchangers have been studied at 25°, 32°, 50° and 65°C under the conditions favourable to the particle diffusion mechanism only. The rate of exchange has been found to be independent of metal ion concentration at and above 0.01 mol dm^{-3} in aqueous medium. Various kinetic parameters such as self-diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation (ΔS) have been calculated.

In continuation of earlier work from our laboratory on the kinetics of exchange of some divalent ions on Zr(IV) arsenophosphate, antimony(V) silicate and zirconium(IV) arsenosilicate, we present herein the results of kinetics of exchange of Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions on zirconium(IV), thorium(IV) and tin(IV) cation exchangers.

Zirconyl chloride, thorium nitrate (both BDH), stannic chloride (P.P.H. Polskie Odezynniki Chemizire Gliwica) and sodium silicate (Reidel) were used as such. All other reagents and chemicals were of AR grade.

Zr(IV) and Th(IV) phosphosilicates (abbreviated as ZPS and TPS respectively) were prepared as follows: To an anaq. solution of sodium silicate (100 ml, 0.1 mol dm^{-3}) were added conc. HCl (50 ml) and aq. zirconium oxychloride solution (1000 ml, 0.1 mol dm^{-3}). The pH of the mixture was kept at 9-10 by adding NH₄OH, the resultant slurry was allowed to stand overnight, filtered, washed with demineralised water (DMW) and mixed with H₃PO₄·HNO₃ mixture (total 1000 ml, 1 mol dm^{-3} each). The gel thus obtained was kept overnight, filtered, washed thoroughly with DMW, dried at 45°C in an air oven and put in DMW to form small granules, which were converted into the H^+ form by treating them with 1 mol dm^{-3} HNO₃.

Thorium(IV) phosphosilicate (TPS) was prepared in a similar manner by taking thorium nitrate, Th(NO₃)₄·6H₂O instead of ZrOCl₂·8H₂O. The Na-ion exchange capacities of the cation exchangers ZPS and TPS were found to be 2.19 and 1.66 meq/dry g respectively.

Sn(IV) arsenosilicate (SAS) was prepared as follows: Decimolar solutions of sodium silicate, sodium arsenate and stannic chloride were mixed in 1:1:1 (v/v) ratio and the pH of the gel adjusted at 1 with HNO₃. It was kept at room temperature for 24 hr, filtered, washed with DMW several times to remove excess reagents, dried at 45°C in an air oven and placed in DMW to form small granules which were converted into the H^+ form by treating with HNO₃ (1 mol dm^{-3}) as usual. The Na-ion exchange capacity for the dried material was found to be 0.95 meq/dry g.

For kinetic measurements aliquots of the metal ion solutions (20 ml) were shaken for different periods with the various mesh-sized particles (25-50, 50-70, 70-100 and 100-150) of the cation exchangers (0.2 g) in a temperature-controlled (± 0.5°C) shaker at different temperatures (25 , 32°, 50°C and 65°C). The supernatant liquids were then removed for the metal ion determinations. To study the concentration effect the metal solutions of varying concentrations (0.005, 0.008, 0.01, 0.05 and 0.1 mol dm^{-3}) were used with the cation exchanger of a definite particle size (average particle radius ~125 μm).

A study of the concentration effect on the rate of exchange at 32°C shows that for Mg^{2+}-H^+ and Mn^{2+}-H^+ exchanges the initial rate of exchange is proportional to the [metal ion] below 0.01 mol dm^{-3} indicating exchange by film diffusion. Above 0.01 mol dm^{-3}, however, the rate of exchange is independent of the [metal ion] indicating that exchange occurs predominantly by particle-diffusion. In this respect the behaviour of exchangers (ZPS, TPS and SAS) is similar to that of other cation exchangers studied earlier.

Although this is a limited bath system, the equation applicable to an infinite bath can be used here because CV ≈ CV', where C and C' are the metal ion concentrations in the solution and exchanger phases respectively and V and V' are the volumes of these two phases. Hence, 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. On the basis of this treatment:

\[ U(\tau) = \left[ 1 - \exp \left\{ \frac{2}{3} \left( f_1(\tau) + f_2(\tau)^2 \right) + f_3(\tau)^3 \right\} \right]^{1/3} \]

where \( \tau = \frac{D_m}{r_0^2} \), and the mobility ratio \( \alpha = \frac{D_n}{D_m} \), \( r_0 \) = particle radius and \( D_m \) is the inter-diffusion coefficient of the metal ion. Under the conditions \( 1 < \alpha \)}
### Table I—Slope of Various T Versus Time Plots as a Function of Temperature and Particle Size of Alkaline Earths and Transition Metals on Zirconium Phosphosilicate

<table>
<thead>
<tr>
<th>Migrating Ion</th>
<th>Particle radius (µm)</th>
<th>25</th>
<th>32</th>
<th>50</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg²⁺</td>
<td>225</td>
<td>1.67</td>
<td>1.33</td>
<td>1.22</td>
<td>0.88</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>125</td>
<td>12.5</td>
<td>13.0</td>
<td>11.6</td>
<td>9.00</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>125</td>
<td>11.1</td>
<td>10.0</td>
<td>9.00</td>
<td>7.00</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>125</td>
<td>7.78</td>
<td>7.00</td>
<td>6.25</td>
<td>5.00</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>225</td>
<td>5.56</td>
<td>5.00</td>
<td>4.33</td>
<td>3.33</td>
</tr>
</tbody>
</table>

Values in circular brackets are for TPS and values in square brackets are for SAS.

**Fig. 1**—Plot of fractional attainment of equilibrium against time for Mg(II) and Mn(II) ions on ZPS.
Table 2—Self-diffusion Coefficient ($D_0$) Energy of Activation ($E_p$) and Entropy of Activation ($\Delta S^\ddagger$) of Alkaline Earths and Transition Metals on Zirconium Phosphosilicate

<table>
<thead>
<tr>
<th>Migrating ion</th>
<th>$10^2$ I onic mobility $(\text{m}^2 \text{V}^{-1} \text{s}^{-1})$</th>
<th>$10^2$ I onic radii (nm)</th>
<th>$D_0$ $(\text{m}^2 \text{s}^{-1})$</th>
<th>$E_p$ $(\text{kJ mol}^{-1})$</th>
<th>$\Delta S^\ddagger$ $(\text{JK}^{-1} \text{mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>55</td>
<td>7.80</td>
<td>$1.9 \times 10^{-6}$</td>
<td>14.53</td>
<td>(63.32)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(1.26 \times 10^{-5})$</td>
<td>(16.20)</td>
<td>(66.76)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(2.51 \times 10^{-5})$</td>
<td>(20.07)</td>
<td>(41.88)</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>62</td>
<td>10.60</td>
<td>$1.91 \times 10^{-6}$</td>
<td>10.02</td>
<td>44.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(2.00 \times 10^{-5})$</td>
<td>(16.41)</td>
<td>(62.93)</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>66</td>
<td>14.30</td>
<td>$1.82 \times 10^{-6}$</td>
<td>31.46</td>
<td>6.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(5.25 \times 10^{-6})$</td>
<td>(18.71)</td>
<td>(54.89)</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>62</td>
<td>12.70</td>
<td>$5.25 \times 10^{-6}$</td>
<td>20.90</td>
<td>35.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(2.03 \times 10^{-6})$</td>
<td>(22.05)</td>
<td>(41.49)</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>55</td>
<td>9.10</td>
<td>$1.66 \times 10^{-6}$</td>
<td>15.78</td>
<td>67.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(4.37 \times 10^{-6})$</td>
<td>(17.56)</td>
<td>(56.43)</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>54</td>
<td>6.70</td>
<td>$1.82 \times 10^{-6}$</td>
<td>26.92</td>
<td>29.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(2.03 \times 10^{-6})$</td>
<td>(20.33)</td>
<td>(51.75)</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>55</td>
<td>8.20</td>
<td>$4.79 \times 10^{-6}$</td>
<td>24.56</td>
<td>67.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(7.94 \times 10^{-6})$</td>
<td>(32.40)</td>
<td>(13.16)</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>52</td>
<td>7.80</td>
<td>$7.24 \times 10^{-6}$</td>
<td>26.92</td>
<td>(13.16)</td>
</tr>
</tbody>
</table>

Values in circular brackets are for TPS and values in square brackets are for SAS

≤20 and the charge ratio $Z_H/Z_M=1/2$, the $\tau$ values were calculated.

A study of the effect of particle size and temperature on the rate of exchange shows that at [metal ion] $= 0.01 \text{ mol dm}^{-3}$ the $\tau$ versus time plots are all linear passing through the origin at all temperatures studied. Also, the slope (Table 1) increases with increase in the particle size which is a fundamental condition for a particle controlled process.

The effect of temperature on the fractional attainment of equilibrium, $U(\tau)$ which is the ratio of the total amount exchanged at time $\tau$ and that at infinite time is illustrated in Fig. 1. It shows that the equilibrium is attained faster at a higher temperature, an observation analogous to other cation exchangers of this class.

The plots of $-\log D_H$ versus $1/T$ are linear and the values of $D_0$, $E_p$ and $\Delta S^\ddagger$ calculated from the plots are summarized in Table 2. A comparison of the results reveals that while for TPS the $E_p$ values are almost the same for all the four alkaline earths, they are widely different for ZPS and SAS. The energy of activation is maximum for Ba$^{2+}$ for exchange on ZPS and SAS indicating greater affinity of these exchangers for this metal ion. It is supported by the fact that separation of Ba$^{2+}$ from Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ has conveniently been achieved on SAS and ZPS columns. The entropy of activation ($\Delta S^\ddagger$) is related to the ionic radii to some extent on SAS for the alkaline earths. For the transition metal ions studied a slightly different behaviour is observed on SAS. As expected, the entropy change is negative for the Mn$^{2+}$-$H^+$ and Co$^{2+}$-$H^+$ exchanges. However, the $\Delta S^\ddagger$ change is positive, for the Fe$^{2+}$-$H^+$ and Ni$^{2+}$-$H^+$ exchanges, probably due to the deformation of the shape of the matrix as a result of exchange processes.

The authors are thankful to Prof. Mohsin Qureshi for research facilities and to the CSIR (New Delhi) for the financial assistance to US and SA.

References
EVALUATION OF THE DIMENSIONLESS TIME PARAMETER FOR SOME PARTICLE DIFFUSION CONTROLLED FORWARD AND REVERSE H(I)—METAL(II) EXCHANGES

K.G. VARSHNEY, KANAK VARSHNEY and SANJAY AGRAWAL
Analytical Laboratories, Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202001 (India)
(Received 31 October 1984; accepted in final form 18 December 1985)

ABSTRACT
The dimensionless time parameter (τ) has been evaluated as a function of fractional exchange of H(I) for some bivalent ions and of the bivalent ions for H(I) using the explicit approximation given by Helfferich et al., applicable to a particle diffusion-controlled ion-exchange process. The calculations have been made using a computer.

INTRODUCTION
Kinetic studies of H(I)—metal-ion exchanges on ion-exchange materials are important for their economic and industrial applications. The B criterion proposed by Boyd et al. [1] is useful for ions having similar effective diffusion coefficients, i.e. for an isotopic exchange process. In a true ion-exchange phenomenon, however, the fluxes of at least two different ionic species are coupled with one another. Thus, a single diffusion coefficient cannot describe the actual process. In such a case, the non-linear Nernst—Planck equations [2, 3] should be applicable for a particle diffusion-controlled ion exchange with some additional assumptions [4]. For practical purposes, an explicit expression was given by Helfferich et al. [5, 6] which approximates the numerical results. Using this expression we have evaluated earlier [7—14] the dimensionless time parameter (τ) for some systems applying the graphical method for its solution. However, the graphical method has been found tedious and gives only the approximate τ values resulting in less accurate kinetic parameters. In view of this the present study has been undertaken to evaluate the τ values for a number of cases involving the exchange of H(I) with bivalent ions using a computer, thus simplifying the treatment and improving the accuracy of the results.
<table>
<thead>
<tr>
<th>Fractional attainment of equilibrium, ( U(\tau) )</th>
<th>Dimensionless time, ( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha = \frac{\bar{D}<em>H}{\bar{D}</em>{Mn}} )</td>
<td>( \alpha = \frac{\bar{D}<em>H}{\bar{D}</em>{Co}} )</td>
</tr>
<tr>
<td>( = 11.39 )</td>
<td>( = 7.42 )</td>
</tr>
<tr>
<td>0.01</td>
<td>2.501 ( \times 10^{-5} )</td>
</tr>
<tr>
<td>0.05</td>
<td>6.262 ( \times 10^{-4} )</td>
</tr>
<tr>
<td>0.10</td>
<td>2.516 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>0.15</td>
<td>5.705 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>0.20</td>
<td>1.026 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.25</td>
<td>1.626 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.30</td>
<td>2.384 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.35</td>
<td>3.315 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.40</td>
<td>4.441 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.45</td>
<td>5.789 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.50</td>
<td>7.395 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.55</td>
<td>9.303 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>0.60</td>
<td>1.157 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.65</td>
<td>1.428 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.70</td>
<td>1.752 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.75</td>
<td>2.143 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.80</td>
<td>2.620 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.85</td>
<td>3.216 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.90</td>
<td>3.990 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.95</td>
<td>5.124 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>0.99</td>
<td>7.067 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>Fractional attainment of equilibrium, $U(\tau)$</td>
<td>Dimensionless time, $\tau$</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>$\alpha = \frac{D_H}{D_{Cd}}$</td>
<td>$\alpha = \frac{D_H}{D_{Za}}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$\tau$</td>
</tr>
<tr>
<td>0.01</td>
<td>$1.971 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.05</td>
<td>$4.933 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.10</td>
<td>$1.982 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.15</td>
<td>$4.494 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.20</td>
<td>$8.075 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.25</td>
<td>$1.279 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.30</td>
<td>$1.875 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.35</td>
<td>$2.605 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.40</td>
<td>$3.488 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.45</td>
<td>$4.544 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.50</td>
<td>$5.800 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.55</td>
<td>$7.292 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.60</td>
<td>$9.066 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.65</td>
<td>$1.119 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.70</td>
<td>$1.374 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.75</td>
<td>$1.683 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.80</td>
<td>$2.066 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.85</td>
<td>$2.549 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.90</td>
<td>$3.191 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.95</td>
<td>$4.152 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.99</td>
<td>$5.832 \times 10^{-1}$</td>
</tr>
<tr>
<td>Fractional attainment of equilibrium, ( U(\tau) )</td>
<td>Dimensionless time, ( \tau )</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>( D_{MN} / D_H )</td>
<td>( D_{Co} / D_H )</td>
</tr>
<tr>
<td>( \alpha = \frac{D_{MN}}{D_H} )</td>
<td>( \alpha = \frac{D_{Co}}{D_H} )</td>
</tr>
<tr>
<td>( \tau = 0.088 )</td>
<td>( \alpha = 0.135 )</td>
</tr>
<tr>
<td>0.01</td>
<td>( 4.360 \times 10^{-6} )</td>
</tr>
<tr>
<td>0.05</td>
<td>( 1.093 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.10</td>
<td>( 4.400 \times 10^{-4} )</td>
</tr>
<tr>
<td>0.15</td>
<td>( 1.004 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.20</td>
<td>( 1.817 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.25</td>
<td>( 2.909 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.30</td>
<td>( 4.319 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.35</td>
<td>( 6.102 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.40</td>
<td>( 8.338 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.45</td>
<td>( 1.113 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.50</td>
<td>( 1.462 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.55</td>
<td>( 1.901 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.60</td>
<td>( 2.449 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.65</td>
<td>( 3.524 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.70</td>
<td>( 3.921 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.75</td>
<td>( 4.981 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.80</td>
<td>( 6.371 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.85</td>
<td>( 8.287 \times 10^{-2} )</td>
</tr>
<tr>
<td>0.90</td>
<td>( 1.169 \times 10^{-1} )</td>
</tr>
<tr>
<td>0.95</td>
<td>( 1.849 \times 10^{-1} )</td>
</tr>
<tr>
<td>0.99</td>
<td>( 3.310 \times 10^{-1} )</td>
</tr>
<tr>
<td>Fractional attainment of equilibrium, $U(\tau)$</td>
<td>Dimensionless time, $\tau$</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>0.01</td>
<td>$4.803 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.05</td>
<td>$1.203 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.10</td>
<td>$4.848 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.15</td>
<td>$1.104 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.20</td>
<td>$1.998 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.25</td>
<td>$3.194 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.30</td>
<td>$4.734 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.35</td>
<td>$6.674 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.40</td>
<td>$9.904 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.45</td>
<td>$1.210 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.50</td>
<td>$1.583 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.55</td>
<td>$2.048 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.60</td>
<td>$2.626 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.65</td>
<td>$3.337 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.70</td>
<td>$4.225 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.75</td>
<td>$5.308 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.80</td>
<td>$6.760 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.85</td>
<td>$8.841 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.90</td>
<td>$1.217 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.95</td>
<td>$1.878 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.99</td>
<td>$3.335 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

According to the explicit approximation given by Heffterich et al. [5, 6], the fractional attainment of equilibrium for a particle diffusion-controlled phenomenon is given by

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

(1)

where \( \tau = \frac{D_A t}{r_0^2} \) and mobility ratio, \( \alpha = \frac{D_A}{D_B} \). The coefficients \( D_A \) and \( D_B \) are the diffusion coefficients of counter ions A and B, respectively, in the ion-exchanger phase, \( r_0 \) is the bead radius and \( t \) is the time. If the ion exchanger is taken in the H(I) form and the exchanging ion is M(II), then for \( 1 \leq \alpha \leq 20 \)

\[ f_1(\alpha) = -\frac{1}{(0.64 + 0.36\alpha^{0.668})} \]
\[ f_2(\alpha) = -\frac{1}{(0.96 - 2.0\alpha^{0.4635})} \]
\[ f_3(\alpha) = -\frac{1}{(0.27 + 0.09\alpha^{1.14})} \]

In the reverse process, i.e. when the ion-exchanger is in the M(II) form and the exchanging ion is H(I), we have

\[ f_1(\alpha) = -\frac{1}{(0.350 + 0.650\alpha^{0.860})} \]
\[ f_2(\alpha) = \frac{1}{(0.030 + 1.012\alpha^{2.06})} \]
\[ f_3(\alpha) = -\frac{1}{(0.00265 + 0.354\alpha^{2.671})} \]

for \( 0.05 \leq \alpha \leq 1 \) and \( 0 \leq \tau \leq 0.04 \), and

\[ f_1(\alpha) = -\frac{1}{(0.438 + 0.562\alpha^{0.777})} \]
\[ f_2(\alpha) = \frac{1}{(0.257 + 0.915\alpha^{1.057})} \]
\[ f_3(\alpha) = \frac{1}{(0.008 - 0.365\alpha^{0.453})} \]

for \( 0.05 \leq \alpha \leq 1 \) and \( \tau \geq 0.04 \).

The \( r \) values obtained from Eqn (1) for the forward and reverse exchange of H(I) with some bivalent metal ions are given in Tables 1 and 2, respectively, for the various fractional exchange values. A computer, Model VAX-11/780 manufactured by the Digital Equipment Corporation, Maynard, MA, was used for calculations.

ACKNOWLEDGEMENTS

Dr Tariq Aziz is thanked for his valuable suggestions and the Council of Scientific and Industrial Research, New Delhi (India) for financial assistance.
REFERENCES

INTRODUCTION

Energy and entropy of activation are the fundamental properties of a system. These parameters are important to understand the mechanism of interactions during the adsorption or ion exchange which are intermixed in case of inorganic ion exchanger. In a true ion exchange phenomenon, different mobilities (1) of the exchanging ions are involved and hence for such a case Nernst-Planck equations (2,3) give the precise values of the various kinetic parameters. For practical purposes, an explicit expression was given by Helfferich et al. (1,4). Using this expression we have evaluated earlier (5-14) the dimensionless time parameter (\( \tau \)) for some systems applying the graphical method for its solution. It was noticed that this method was very tedious and gave only the approximate \( \tau \) values. A computer simulation technique has,
therefore, been used. On the basis of which we have earlier reported (15) the \( \tau \) values for the particle diffusion controlled forward and reverse \( \text{H(I)-Metal(II)} \) ion exchanges. In continuation we, here, report the \( \tau \) values obtained for the exchange of \( \text{OH(I)} \) ions with some common mono- and bi-valent anions, using a computer which improves the results accuracy. A knowledge of \( \tau \) values for the various mobility ratios is very important and makes the calculations much easier for the evaluation of the kinetic parameters. The present report will help in the study of anion exchanges.

RESULTS AND DISCUSSION

According to the explicit approximation given by Helferrich et al. (1,4) the fractional attainment of equilibrium for a particle diffusion controlled phenomenon is given by

\[
U(\tau) = \left[ 1 - \exp \left( \frac{2}{\lambda} \left( f_1 (\lambda) \tau + f_2 (\lambda) \tau^2 + f_3 (\lambda) \tau^3 \right) \right) \right]^{\frac{1}{2}}
\]

(1)

where \( \tau = \bar{D}_A t / r_0 \) and \( \lambda = \bar{D}_A / \bar{D}_B \). The coefficients \( \bar{D}_A \) and \( \bar{D}_B \) are the diffusion coefficients of counter ions A and B respectively in the ion exchanger phase, \( r_0 \) is the bead radius and \( t \) is the time.

For monovalent anions A(I): A monovalent anion exchange phenomenon may be expressed as follows:

\[
\text{R}^+\text{OH}^- + \text{A}^- \rightleftharpoons \text{R}^+\text{A}^- + \text{OH}^- 
\]
For the above process both in the forward and reverse directions
the coefficients are given by

\[ f_1(\alpha) = \frac{1}{0.57 + 0.43\alpha^{0.775}} \]
\[ f_2(\alpha) = \frac{1}{0.26 + 0.788\alpha} \]
\[ f_3(\alpha) = \frac{1}{0.165 + 0.177\alpha} \]

for a range of validity \(0.1 \leq \alpha \leq 10\).

For bivalent anions: A bivalent anion exchange equation may be
given as

\[ 2R^+\text{OH}^- + A^{2-} \rightleftharpoons R_2^+A^{2-} + 2\text{OH}^- \]

For the forward process i.e. if the ion exchanger is taken in OH(I)
form and the exchanging ion is A(II) then the coefficients are
given by for a range of \(1 \leq \alpha \leq 20\)

\[ f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}} \]
\[ f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}} \]
\[ f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.14}} \]

and for the reverse process i.e. when the ion exchanger is in A(II)
form and the exchanging ion is OH(I) then we have

\[ f_1(\alpha) = -\frac{1}{0.35 + 0.65\alpha^{0.86}} \]
\[ f_2(\alpha) = -\frac{1}{0.03 + 1.012\alpha^{2.06}} \]
\[ f_3(\alpha) = -\frac{1}{0.00265 + 0.354\alpha^{2.671}} \]

for the range of \(0.05 \leq \alpha \leq 1\) and \(0 \leq T \leq 0.04\) and
\( f_1(\alpha) = \frac{-1}{0.438 + 0.562 \alpha^{0.777}} \)
\( f_2(\alpha) = \frac{1}{0.127 + 0.915 \alpha^{1.057}} \)
\( f_3(\alpha) = \frac{1}{0.008 - 0.365 \alpha^{0.453}} \)
for \( 0.05 \leq \alpha \leq 1 \) and \( \tau > 0.04 \)

The values obtained from equation (1) for the forward and reverse exchange of OH(I) with some monovalent and bivalent anions are given in Tables 1-4 respectively for the various fractional exchange values. A computer, model VAX 11/780 manufactured by the digital equipment corporation, Maynard, MA was used for these calculations.

ACKNOWLEDGEMENT

Prof. K.T. Nasim, Chairman, Department of Applied Chemistry and Director of Computer Centre, Aligarh Muslim University, Aligarh are thanked for providing research facilities.

REFERENCES


<table>
<thead>
<tr>
<th>Fractional attainment of equilibrium U(τ)</th>
<th>Dimensionless time, τ</th>
</tr>
</thead>
</table>
|                                          | \( \frac{\tilde{D}_{OH}}{D_{IO_3}} \) | \( \frac{\tilde{D}_{OH}}{D_{F}} \) | \( \frac{\tilde{D}_{OH}}{D_{BrO_3}} \) | \( \frac{\tilde{D}_{OH}}{D_{MnO_4}} \) | \( \frac{\tilde{D}_{OH}}{D_{CIO_3/}
CNO/OCN} \) | \( \frac{\tilde{D}_{OH}}{D_{SCN}} \) | \( \frac{\tilde{D}_{OH}}{D_{ClO_4}} \) |  |
| 0.01                                      | 2.068 x 10^{-5}     | 1.747 x 10^{-5}     | 1.742 x 10^{-5}     | 1.659 x 10^{-5}     | 1.616 x 10^{-5}     | 1.599 x 10^{-5}     | 1.583 x 10^{-5}     |  |
| 0.05                                      | 5.178 x 10^{-4}     | 4.373 x 10^{-4}     | 4.360 x 10^{-4}     | 4.152 x 10^{-4}     | 4.045 x 10^{-4}     | 4.002 x 10^{-4}     | 3.963 x 10^{-4}     |  |
| 0.10                                      | 2.081 x 10^{-3}     | 1.757 x 10^{-3}     | 1.752 x 10^{-3}     | 1.668 x 10^{-3}     | 1.625 x 10^{-3}     | 1.606 x 10^{-3}     | 1.593 x 10^{-3}     |  |
| 0.15                                      | 4.717 x 10^{-3}     | 3.984 x 10^{-3}     | 3.972 x 10^{-3}     | 3.782 x 10^{-3}     | 3.684 x 10^{-3}     | 3.645 x 10^{-3}     | 3.610 x 10^{-3}     |  |
| 0.20                                      | 8.477 x 10^{-3}     | 7.158 x 10^{-3}     | 7.139 x 10^{-3}     | 6.797 x 10^{-3}     | 6.620 x 10^{-3}     | 6.550 x 10^{-3}     | 6.687 x 10^{-3}     |  |
| 0.25                                      | 1.343 x 10^{-2}     | 1.134 x 10^{-2}     | 1.131 x 10^{-2}     | 1.077 x 10^{-2}     | 1.049 x 10^{-2}     | 1.038 x 10^{-2}     | 1.028 x 10^{-2}     |  |
| 0.30                                      | 1.968 x 10^{-2}     | 1.662 x 10^{-2}     | 1.657 x 10^{-2}     | 1.578 x 10^{-2}     | 1.537 x 10^{-2}     | 1.521 x 10^{-2}     | 1.506 x 10^{-2}     |  |
| 0.35                                      | 2.736 x 10^{-2}     | 2.310 x 10^{-2}     | 2.305 x 10^{-2}     | 2.193 x 10^{-2}     | 2.156 x 10^{-2}     | 2.114 x 10^{-2}     | 2.093 x 10^{-2}     |  |
| 0.40                                      | 3.663 x 10^{-2}     | 3.093 x 10^{-2}     | 3.084 x 10^{-2}     | 2.937 x 10^{-2}     | 2.860 x 10^{-2}     | 2.830 x 10^{-2}     | 2.803 x 10^{-2}     |  |
| 0.45                                      | 4.772 x 10^{-2}     | 4.030 x 10^{-2}     | 4.018 x 10^{-2}     | 3.826 x 10^{-2}     | 3.727 x 10^{-2}     | 3.688 x 10^{-2}     | 3.652 x 10^{-2}     |  |
| 0.50                                      | 6.092 x 10^{-2}     | 5.145 x 10^{-2}     | 5.130 x 10^{-2}     | 4.885 x 10^{-2}     | 4.759 x 10^{-2}     | 4.709 x 10^{-2}     | 4.664 x 10^{-2}     |  |
| 0.55                                      | 7.654 x 10^{-2}     | 6.470 x 10^{-2}     | 6.451 x 10^{-2}     | 6.145 x 10^{-2}     | 5.986 x 10^{-2}     | 5.923 x 10^{-2}     | 5.867 x 10^{-2}     |  |
| 0.60                                      | 9.511 x 10^{-2}     | 8.048 x 10^{-2}     | 8.025 x 10^{-2}     | 7.646 x 10^{-2}     | 7.449 x 10^{-2}     | 7.371 x 10^{-2}     | 7.301 x 10^{-2}     |  |
| 0.65                                      | 1.172 x 10^{-1}     | 9.935 x 10^{-2}     | 9.907 x 10^{-2}     | 9.443 x 10^{-2}     | 9.202 x 10^{-2}     | 9.106 x 10^{-2}     | 9.021 x 10^{-2}     |  |
| 0.70                                      | 1.437 x 10^{-1}     | 1.221 x 10^{-1}     | 1.217 x 10^{-1}     | 1.161 x 10^{-1}     | 1.132 x 10^{-1}     | 1.120 x 10^{-1}     | 1.110 x 10^{-1}     |  |
| 0.75                                      | 1.756 x 10^{-1}     | 1.498 x 10^{-1}     | 1.494 x 10^{-1}     | 1.426 x 10^{-1}     | 1.391 x 10^{-1}     | 1.377 x 10^{-1}     | 1.364 x 10^{-1}     |  |
| 0.80                                      | 2.147 x 10^{-1}     | 1.841 x 10^{-1}     | 1.836 x 10^{-1}     | 1.755 x 10^{-1}     | 1.715 x 10^{-1}     | 1.696 x 10^{-1}     | 1.661 x 10^{-1}     |  |
| 0.85                                      | 2.656 x 10^{-1}     | 2.277 x 10^{-1}     | 2.271 x 10^{-1}     | 2.175 x 10^{-1}     | 2.175 x 10^{-1}     | 2.106 x 10^{-1}     | 2.088 x 10^{-1}     |  |
| 0.90                                      | 3.275 x 10^{-1}     | 2.857 x 10^{-1}     | 2.850 x 10^{-1}     | 2.739 x 10^{-1}     | 2.680 x 10^{-1}     | 2.657 x 10^{-1}     | 2.636 x 10^{-1}     |  |
| 0.95                                      | 4.217 x 10^{-1}     | 3.780 x 10^{-1}     | 3.722 x 10^{-1}     | 3.590 x 10^{-1}     | 3.521 x 10^{-1}     | 3.493 x 10^{-1}     | 3.468 x 10^{-1}     |  |
| 0.99                                      | 5.848 x 10^{-1}     | 5.259 x 10^{-1}     | 5.249 x 10^{-1}     | 5.089 x 10^{-1}     | 5.005 x 10^{-1}     | 4.972 x 10^{-1}     | 4.941 x 10^{-1}     |  |
(Table 1 continued)

<table>
<thead>
<tr>
<th>Fractional attainment of equilibrium (U(T))</th>
<th>(\lambda = \frac{D_{OH}}{D_{NO_3}})</th>
<th>(\lambda = \frac{D_{OH}}{D_{NO_2}})</th>
<th>(\lambda = \frac{D_{OH}}{D_{Cl}})</th>
<th>(\lambda = \frac{D_{OH}}{D_{I}})</th>
<th>(\lambda = \frac{D_{OH}}{D_{CN}})</th>
<th>(\lambda = \frac{D_{OH}}{D_{Br}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>1.538x10^-5</td>
<td>1.534x10^-5</td>
<td>1.490x10^-5</td>
<td>1.486x10^-5</td>
<td>1.475x10^-5</td>
<td>1.474x10^-5</td>
</tr>
<tr>
<td>0.05</td>
<td>3.850x10^-4</td>
<td>3.848x10^-4</td>
<td>3.750x10^-4</td>
<td>3.718x10^-4</td>
<td>3.691x10^-4</td>
<td>3.689x10^-4</td>
</tr>
<tr>
<td>0.10</td>
<td>1.547x10^-3</td>
<td>1.543x10^-3</td>
<td>1.499x10^-3</td>
<td>1.494x10^-3</td>
<td>1.483x10^-3</td>
<td>1.482x10^-3</td>
</tr>
<tr>
<td>0.15</td>
<td>3.507x10^-3</td>
<td>3.498x10^-3</td>
<td>3.398x10^-3</td>
<td>3.378x10^-3</td>
<td>3.362x10^-3</td>
<td>3.356x10^-3</td>
</tr>
<tr>
<td>0.20</td>
<td>6.301x10^-3</td>
<td>6.285x10^-3</td>
<td>6.105x10^-3</td>
<td>6.086x10^-3</td>
<td>6.041x10^-3</td>
<td>6.038x10^-3</td>
</tr>
<tr>
<td>0.25</td>
<td>9.984x10^-3</td>
<td>9.958x10^-3</td>
<td>9.673x10^-3</td>
<td>9.643x10^-3</td>
<td>9.572x10^-3</td>
<td>9.566x10^-3</td>
</tr>
<tr>
<td>0.30</td>
<td>1.463x10^-2</td>
<td>1.459x10^-2</td>
<td>1.417x10^-2</td>
<td>1.413x10^-2</td>
<td>1.402x10^-2</td>
<td>1.402x10^-2</td>
</tr>
<tr>
<td>0.35</td>
<td>2.033x10^-2</td>
<td>2.028x10^-2</td>
<td>1.970x10^-2</td>
<td>1.964x10^-2</td>
<td>1.949x10^-2</td>
<td>1.948x10^-2</td>
</tr>
<tr>
<td>0.40</td>
<td>2.723x10^-2</td>
<td>2.716x10^-2</td>
<td>2.638x10^-2</td>
<td>2.630x10^-2</td>
<td>2.610x10^-2</td>
<td>2.609x10^-2</td>
</tr>
<tr>
<td>0.45</td>
<td>3.548x10^-2</td>
<td>3.538x10^-2</td>
<td>3.437x10^-2</td>
<td>3.427x10^-2</td>
<td>3.401x10^-2</td>
<td>3.400x10^-2</td>
</tr>
<tr>
<td>0.50</td>
<td>4.530x10^-2</td>
<td>4.519x10^-2</td>
<td>4.390x10^-2</td>
<td>4.376x10^-2</td>
<td>4.344x10^-2</td>
<td>4.342x10^-2</td>
</tr>
<tr>
<td>0.55</td>
<td>5.700x10^-2</td>
<td>5.685x10^-2</td>
<td>5.523x10^-2</td>
<td>5.506x10^-2</td>
<td>5.466x10^-2</td>
<td>5.463x10^-2</td>
</tr>
<tr>
<td>0.60</td>
<td>7.094x10^-2</td>
<td>7.076x10^-2</td>
<td>6.876x10^-2</td>
<td>6.855x10^-2</td>
<td>6.805x10^-2</td>
<td>6.801x10^-2</td>
</tr>
<tr>
<td>0.65</td>
<td>8.767x10^-2</td>
<td>8.744x10^-2</td>
<td>8.499x10^-2</td>
<td>8.473x10^-2</td>
<td>8.412x10^-2</td>
<td>8.407x10^-2</td>
</tr>
<tr>
<td>0.70</td>
<td>1.079x10^-1</td>
<td>1.076x10^-1</td>
<td>1.047x10^-1</td>
<td>1.043x10^-1</td>
<td>1.036x10^-1</td>
<td>1.035x10^-1</td>
</tr>
<tr>
<td>0.75</td>
<td>1.327x10^-1</td>
<td>1.324x10^-1</td>
<td>1.288x10^-1</td>
<td>1.284x10^-1</td>
<td>1.275x10^-1</td>
<td>1.274x10^-1</td>
</tr>
<tr>
<td>0.80</td>
<td>1.637x10^-1</td>
<td>1.633x10^-1</td>
<td>1.590x10^-1</td>
<td>1.585x10^-1</td>
<td>1.574x10^-1</td>
<td>1.574x10^-1</td>
</tr>
<tr>
<td>0.85</td>
<td>2.035x10^-1</td>
<td>2.030x10^-1</td>
<td>1.979x10^-1</td>
<td>1.973x10^-1</td>
<td>1.961x10^-1</td>
<td>1.960x10^-1</td>
</tr>
<tr>
<td>0.90</td>
<td>2.573x10^-1</td>
<td>2.568x10^-1</td>
<td>2.507x10^-1</td>
<td>2.500x10^-1</td>
<td>2.485x10^-1</td>
<td>2.484x10^-1</td>
</tr>
<tr>
<td>0.95</td>
<td>3.394x10^-1</td>
<td>3.388x10^-1</td>
<td>3.316x10^-1</td>
<td>3.308x10^-1</td>
<td>3.290x10^-1</td>
<td>3.289x10^-1</td>
</tr>
<tr>
<td>0.99</td>
<td>4.851x10^-1</td>
<td>4.843x10^-1</td>
<td>4.755x10^-1</td>
<td>4.746x10^-1</td>
<td>4.724x10^-1</td>
<td>4.722x10^-1</td>
</tr>
<tr>
<td>1.00</td>
<td>6.378x10^-1</td>
<td>6.372x10^-1</td>
<td>6.284x10^-1</td>
<td>6.273x10^-1</td>
<td>6.250x10^-1</td>
<td>6.246x10^-1</td>
</tr>
<tr>
<td>Fractional attainment of equilibrium $U(\tau)$</td>
<td>Dimensionless time, $\tau$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>-----------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_{IO_3} \cdot \frac{\lambda}{D_{OH}}$</td>
<td>$D_F \cdot \frac{\lambda}{D_{OH}}$</td>
<td>$D_{BrO_3} \cdot \frac{\lambda}{D_{OH}}$</td>
<td>$D_{MnO_4} \cdot \frac{\lambda}{D_{OH}}$</td>
<td>$D_{C10_2/ClO_3/0CN} \cdot \frac{\lambda}{D_{OH}}$</td>
<td>$D_{SCN} \cdot \frac{\lambda}{D_{OH}}$</td>
</tr>
<tr>
<td>0.01</td>
<td>7.048x10^{-6}</td>
<td>7.397x10^{-6}</td>
<td>7.406x10^{-6}</td>
<td>7.530x10^{-6}</td>
<td>7.605x10^{-6}</td>
<td>7.639x10^{-6}</td>
</tr>
<tr>
<td>0.05</td>
<td>1.764x10^{-4}</td>
<td>1.852x10^{-4}</td>
<td>1.854x10^{-4}</td>
<td>1.885x10^{-4}</td>
<td>1.904x10^{-4}</td>
<td>1.912x10^{-4}</td>
</tr>
<tr>
<td>0.10</td>
<td>7.090x10^{-4}</td>
<td>7.441x10^{-4}</td>
<td>7.450x10^{-4}</td>
<td>7.575x10^{-4}</td>
<td>7.650x10^{-4}</td>
<td>7.685x10^{-4}</td>
</tr>
<tr>
<td>0.15</td>
<td>1.608x10^{-3}</td>
<td>1.687x10^{-3}</td>
<td>1.689x10^{-3}</td>
<td>1.718x10^{-3}</td>
<td>1.735x10^{-3}</td>
<td>1.742x10^{-3}</td>
</tr>
<tr>
<td>0.20</td>
<td>2.890x10^{-3}</td>
<td>3.033x10^{-3}</td>
<td>3.057x10^{-3}</td>
<td>3.087x10^{-3}</td>
<td>3.118x10^{-3}</td>
<td>3.132x10^{-3}</td>
</tr>
<tr>
<td>0.25</td>
<td>4.582x10^{-3}</td>
<td>4.808x10^{-3}</td>
<td>4.814x10^{-3}</td>
<td>4.894x10^{-3}</td>
<td>4.942x10^{-3}</td>
<td>4.964x10^{-3}</td>
</tr>
<tr>
<td>0.30</td>
<td>6.719x10^{-3}</td>
<td>7.049x10^{-3}</td>
<td>7.058x10^{-3}</td>
<td>7.175x10^{-3}</td>
<td>7.246x10^{-3}</td>
<td>7.278x10^{-3}</td>
</tr>
<tr>
<td>0.35</td>
<td>9.350x10^{-3}</td>
<td>9.808x10^{-3}</td>
<td>9.819x10^{-3}</td>
<td>9.983x10^{-3}</td>
<td>1.008x10^{-2}</td>
<td>1.013x10^{-2}</td>
</tr>
<tr>
<td>0.40</td>
<td>1.254x10^{-2}</td>
<td>1.315x10^{-2}</td>
<td>1.317x10^{-2}</td>
<td>1.358x10^{-2}</td>
<td>1.351x10^{-2}</td>
<td>1.357x10^{-2}</td>
</tr>
<tr>
<td>0.45</td>
<td>1.637x10^{-2}</td>
<td>1.717x10^{-2}</td>
<td>1.719x10^{-2}</td>
<td>1.747x10^{-2}</td>
<td>1.764x10^{-2}</td>
<td>1.772x10^{-2}</td>
</tr>
<tr>
<td>0.50</td>
<td>2.097x10^{-2}</td>
<td>2.198x10^{-2}</td>
<td>2.200x10^{-2}</td>
<td>2.236x10^{-2}</td>
<td>2.258x10^{-2}</td>
<td>2.268x10^{-2}</td>
</tr>
<tr>
<td>0.55</td>
<td>2.648x10^{-2}</td>
<td>2.774x10^{-2}</td>
<td>2.778x10^{-2}</td>
<td>2.823x10^{-2}</td>
<td>2.850x10^{-2}</td>
<td>2.862x10^{-2}</td>
</tr>
<tr>
<td>0.60</td>
<td>3.314x10^{-2}</td>
<td>3.470x10^{-2}</td>
<td>3.474x10^{-2}</td>
<td>3.530x10^{-2}</td>
<td>3.563x10^{-2}</td>
<td>3.578x10^{-2}</td>
</tr>
<tr>
<td>0.65</td>
<td>4.127x10^{-2}</td>
<td>4.317x10^{-2}</td>
<td>4.322x10^{-2}</td>
<td>4.391x10^{-2}</td>
<td>4.431x10^{-2}</td>
<td>4.450x10^{-2}</td>
</tr>
<tr>
<td>0.70</td>
<td>5.135x10^{-2}</td>
<td>5.367x10^{-2}</td>
<td>5.373x10^{-2}</td>
<td>5.455x10^{-2}</td>
<td>5.505x10^{-2}</td>
<td>5.528x10^{-2}</td>
</tr>
<tr>
<td>0.75</td>
<td>6.416x10^{-2}</td>
<td>6.696x10^{-2}</td>
<td>6.703x10^{-2}</td>
<td>6.803x10^{-2}</td>
<td>6.863x10^{-2}</td>
<td>6.891x10^{-2}</td>
</tr>
<tr>
<td>0.80</td>
<td>8.105x10^{-2}</td>
<td>8.438x10^{-2}</td>
<td>8.446x10^{-2}</td>
<td>8.566x10^{-2}</td>
<td>8.638x10^{-2}</td>
<td>8.671x10^{-2}</td>
</tr>
<tr>
<td>0.85</td>
<td>1.045x10^{-1}</td>
<td>1.094x10^{-1}</td>
<td>1.085x10^{-1}</td>
<td>1.099x10^{-1}</td>
<td>1.108x10^{-1}</td>
<td>1.112x10^{-1}</td>
</tr>
<tr>
<td>0.90</td>
<td>1.400x10^{-1}</td>
<td>1.444x10^{-1}</td>
<td>1.445x10^{-1}</td>
<td>1.461x10^{-1}</td>
<td>1.471x10^{-1}</td>
<td>1.475x10^{-1}</td>
</tr>
<tr>
<td>0.95</td>
<td>2.035x10^{-1}</td>
<td>2.074x10^{-1}</td>
<td>2.076x10^{-1}</td>
<td>2.091x10^{-1}</td>
<td>2.101x10^{-1}</td>
<td>2.105x10^{-1}</td>
</tr>
<tr>
<td>0.99</td>
<td>3.322x10^{-1}</td>
<td>3.332x10^{-1}</td>
<td>3.332x10^{-1}</td>
<td>3.341x10^{-1}</td>
<td>3.347x10^{-1}</td>
<td>3.350x10^{-1}</td>
</tr>
<tr>
<td>Fractional attainment of equilibrium $U(\tau)$</td>
<td>Dimensionless time, $\tau$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>-----------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda = \frac{D_{\text{NO}<em>2}}{D</em>{\text{OH}}}$</td>
<td>$\lambda = \frac{D_{\text{NO}<em>2}}{D</em>{\text{OH}}}$</td>
<td>$\lambda = \frac{D_{\text{Cl}}}{D_{\text{OH}}}$</td>
<td>$\lambda = \frac{D_{\text{I}}}{D_{\text{OH}}}$</td>
<td>$\lambda = \frac{D_{\text{CN}}}{D_{\text{OH}}}$</td>
<td>$\lambda = \frac{D_{\text{Br}}}{D_{\text{OH}}}$</td>
<td></td>
</tr>
<tr>
<td>$= 0.361$</td>
<td>$= 0.363$</td>
<td>$= 0.385$</td>
<td>$= 0.387$</td>
<td>$= 0.394$</td>
<td>$= 0.395$</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>$7.755 \times 10^{-6}$</td>
<td>$7.764 \times 10^{-6}$</td>
<td>$7.856 \times 10^{-6}$</td>
<td>$7.865 \times 10^{-6}$</td>
<td>$7.898 \times 10^{-6}$</td>
<td>$7.898 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.05</td>
<td>$1.941 \times 10^{-4}$</td>
<td>$1.943 \times 10^{-4}$</td>
<td>$1.967 \times 10^{-4}$</td>
<td>$1.969 \times 10^{-4}$</td>
<td>$1.976 \times 10^{-4}$</td>
<td>$1.977 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.10</td>
<td>$7.801 \times 10^{-4}$</td>
<td>$7.809 \times 10^{-4}$</td>
<td>$7.903 \times 10^{-4}$</td>
<td>$7.911 \times 10^{-4}$</td>
<td>$7.940 \times 10^{-4}$</td>
<td>$7.945 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.15</td>
<td>$1.769 \times 10^{-3}$</td>
<td>$1.771 \times 10^{-3}$</td>
<td>$1.792 \times 10^{-3}$</td>
<td>$1.794 \times 10^{-3}$</td>
<td>$1.800 \times 10^{-3}$</td>
<td>$1.801 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.20</td>
<td>$3.179 \times 10^{-3}$</td>
<td>$3.183 \times 10^{-3}$</td>
<td>$3.221 \times 10^{-3}$</td>
<td>$3.224 \times 10^{-3}$</td>
<td>$3.256 \times 10^{-3}$</td>
<td>$3.238 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.25</td>
<td>$5.039 \times 10^{-3}$</td>
<td>$5.045 \times 10^{-3}$</td>
<td>$5.105 \times 10^{-3}$</td>
<td>$5.110 \times 10^{-3}$</td>
<td>$5.129 \times 10^{-3}$</td>
<td>$5.132 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.30</td>
<td>$7.388 \times 10^{-3}$</td>
<td>$7.396 \times 10^{-3}$</td>
<td>$7.484 \times 10^{-3}$</td>
<td>$7.492 \times 10^{-3}$</td>
<td>$7.519 \times 10^{-3}$</td>
<td>$7.523 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.35</td>
<td>$1.028 \times 10^{-2}$</td>
<td>$1.029 \times 10^{-2}$</td>
<td>$1.041 \times 10^{-2}$</td>
<td>$1.042 \times 10^{-2}$</td>
<td>$1.046 \times 10^{-2}$</td>
<td>$1.046 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.40</td>
<td>$1.378 \times 10^{-2}$</td>
<td>$1.379 \times 10^{-2}$</td>
<td>$1.395 \times 10^{-2}$</td>
<td>$1.397 \times 10^{-2}$</td>
<td>$1.402 \times 10^{-2}$</td>
<td>$1.403 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.45</td>
<td>$1.798 \times 10^{-2}$</td>
<td>$1.800 \times 10^{-2}$</td>
<td>$1.821 \times 10^{-2}$</td>
<td>$1.823 \times 10^{-2}$</td>
<td>$1.830 \times 10^{-2}$</td>
<td>$1.831 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.50</td>
<td>$2.301 \times 10^{-2}$</td>
<td>$2.304 \times 10^{-2}$</td>
<td>$2.330 \times 10^{-2}$</td>
<td>$2.333 \times 10^{-2}$</td>
<td>$2.341 \times 10^{-2}$</td>
<td>$2.343 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.55</td>
<td>$2.904 \times 10^{-2}$</td>
<td>$2.907 \times 10^{-2}$</td>
<td>$2.941 \times 10^{-2}$</td>
<td>$2.944 \times 10^{-2}$</td>
<td>$2.954 \times 10^{-2}$</td>
<td>$2.956 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.60</td>
<td>$3.630 \times 10^{-2}$</td>
<td>$3.634 \times 10^{-2}$</td>
<td>$3.676 \times 10^{-2}$</td>
<td>$3.679 \times 10^{-2}$</td>
<td>$3.692 \times 10^{-2}$</td>
<td>$3.694 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.65</td>
<td>$4.514 \times 10^{-2}$</td>
<td>$4.518 \times 10^{-2}$</td>
<td>$4.569 \times 10^{-2}$</td>
<td>$4.574 \times 10^{-2}$</td>
<td>$4.590 \times 10^{-2}$</td>
<td>$4.592 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.70</td>
<td>$5.605 \times 10^{-2}$</td>
<td>$5.611 \times 10^{-2}$</td>
<td>$5.673 \times 10^{-2}$</td>
<td>$5.678 \times 10^{-2}$</td>
<td>$5.698 \times 10^{-2}$</td>
<td>$5.701 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.75</td>
<td>$6.984 \times 10^{-2}$</td>
<td>$6.991 \times 10^{-2}$</td>
<td>$7.066 \times 10^{-2}$</td>
<td>$7.072 \times 10^{-2}$</td>
<td>$7.096 \times 10^{-2}$</td>
<td>$7.099 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.80</td>
<td>$8.787 \times 10^{-2}$</td>
<td>$8.792 \times 10^{-2}$</td>
<td>$8.882 \times 10^{-2}$</td>
<td>$8.890 \times 10^{-2}$</td>
<td>$8.918 \times 10^{-2}$</td>
<td>$8.922 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.85</td>
<td>$1.125 \times 10^{-1}$</td>
<td>$1.126 \times 10^{-1}$</td>
<td>$1.137 \times 10^{-1}$</td>
<td>$1.138 \times 10^{-1}$</td>
<td>$1.141 \times 10^{-1}$</td>
<td>$1.141 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.90</td>
<td>$1.490 \times 10^{-1}$</td>
<td>$1.492 \times 10^{-1}$</td>
<td>$1.504 \times 10^{-1}$</td>
<td>$1.505 \times 10^{-1}$</td>
<td>$1.509 \times 10^{-1}$</td>
<td>$1.509 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.95</td>
<td>$2.121 \times 10^{-1}$</td>
<td>$2.122 \times 10^{-1}$</td>
<td>$2.135 \times 10^{-1}$</td>
<td>$2.136 \times 10^{-1}$</td>
<td>$2.140 \times 10^{-1}$</td>
<td>$2.140 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.99</td>
<td>$3.362 \times 10^{-1}$</td>
<td>$3.363 \times 10^{-1}$</td>
<td>$3.373 \times 10^{-1}$</td>
<td>$3.374 \times 10^{-1}$</td>
<td>$3.377 \times 10^{-1}$</td>
<td>$3.378 \times 10^{-1}$</td>
</tr>
<tr>
<td>Fractional attainment of equilibrium ( U(\tau) )</td>
<td>Dimensionless time, ( \tau )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{D_{OH}}{D_{HP0}_4} )</td>
<td>( \frac{D_{OH}}{D_{S0}_2} )</td>
<td>( \frac{D_{OH}}{D_{CO}_3} )</td>
<td>( \frac{D_{OH}}{D_{NO}_4} )</td>
<td>( \frac{D_{OH}}{D_{C0}_2} )</td>
<td>( \frac{D_{OH}}{D_{Se0}_4} )</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>1.856x10^{-5}</td>
<td>1.405x10^{-5}</td>
<td>1.395x10^{-5}</td>
<td>1.386x10^{-5}</td>
<td>1.369x10^{-5}</td>
<td>1.342x10^{-5}</td>
</tr>
<tr>
<td>0.05</td>
<td>4.646x10^{-4}</td>
<td>3.516x10^{-4}</td>
<td>3.492x10^{-4}</td>
<td>3.417x10^{-4}</td>
<td>3.427x10^{-4}</td>
<td>3.359x10^{-4}</td>
</tr>
<tr>
<td>0.10</td>
<td>1.867x10^{-3}</td>
<td>1.413x10^{-3}</td>
<td>1.403x10^{-3}</td>
<td>1.394x10^{-3}</td>
<td>1.377x10^{-3}</td>
<td>1.350x10^{-3}</td>
</tr>
<tr>
<td>0.15</td>
<td>4.232x10^{-3}</td>
<td>3.202x10^{-3}</td>
<td>3.180x10^{-3}</td>
<td>3.160x10^{-3}</td>
<td>3.121x10^{-3}</td>
<td>3.059x10^{-3}</td>
</tr>
<tr>
<td>0.20</td>
<td>7.604x10^{-3}</td>
<td>5.752x10^{-3}</td>
<td>5.712x10^{-3}</td>
<td>5.677x10^{-3}</td>
<td>5.606x10^{-3}</td>
<td>5.495x10^{-3}</td>
</tr>
<tr>
<td>0.25</td>
<td>1.205x10^{-2}</td>
<td>9.111x10^{-3}</td>
<td>9.048x10^{-3}</td>
<td>8.991x10^{-3}</td>
<td>8.880x10^{-3}</td>
<td>8.704x10^{-3}</td>
</tr>
<tr>
<td>0.30</td>
<td>1.765x10^{-2}</td>
<td>1.534x10^{-2}</td>
<td>1.325x10^{-2}</td>
<td>1.517x10^{-2}</td>
<td>1.301x10^{-2}</td>
<td>1.275x10^{-2}</td>
</tr>
<tr>
<td>0.35</td>
<td>2.453x10^{-2}</td>
<td>1.854x10^{-2}</td>
<td>1.841x10^{-2}</td>
<td>1.830x10^{-2}</td>
<td>1.807x10^{-2}</td>
<td>1.771x10^{-2}</td>
</tr>
<tr>
<td>0.40</td>
<td>3.283x10^{-2}</td>
<td>2.481x10^{-2}</td>
<td>2.464x10^{-2}</td>
<td>2.449x10^{-2}</td>
<td>2.418x10^{-2}</td>
<td>2.370x10^{-2}</td>
</tr>
<tr>
<td>0.45</td>
<td>4.276x10^{-2}</td>
<td>3.231x10^{-2}</td>
<td>3.209x10^{-2}</td>
<td>3.189x10^{-2}</td>
<td>3.149x10^{-2}</td>
<td>3.087x10^{-2}</td>
</tr>
<tr>
<td>0.50</td>
<td>5.458x10^{-2}</td>
<td>4.124x10^{-2}</td>
<td>4.095x10^{-2}</td>
<td>4.069x10^{-2}</td>
<td>4.019x10^{-2}</td>
<td>3.940x10^{-2}</td>
</tr>
<tr>
<td>0.55</td>
<td>6.862x10^{-2}</td>
<td>5.184x10^{-2}</td>
<td>5.149x10^{-2}</td>
<td>5.116x10^{-2}</td>
<td>5.054x10^{-2}</td>
<td>4.954x10^{-2}</td>
</tr>
<tr>
<td>0.60</td>
<td>8.531x10^{-2}</td>
<td>6.448x10^{-2}</td>
<td>6.404x10^{-2}</td>
<td>6.364x10^{-2}</td>
<td>6.286x10^{-2}</td>
<td>6.165x10^{-2}</td>
</tr>
<tr>
<td>0.65</td>
<td>1.053x10^{-1}</td>
<td>7.964x10^{-2}</td>
<td>7.909x10^{-2}</td>
<td>7.860x10^{-2}</td>
<td>7.765x10^{-2}</td>
<td>7.613x10^{-2}</td>
</tr>
<tr>
<td>0.70</td>
<td>1.293x10^{-1}</td>
<td>9.797x10^{-2}</td>
<td>9.731x10^{-2}</td>
<td>9.671x10^{-2}</td>
<td>9.555x10^{-2}</td>
<td>9.370x10^{-2}</td>
</tr>
<tr>
<td>0.75</td>
<td>1.585x10^{-1}</td>
<td>1.205x10^{-1}</td>
<td>1.197x10^{-1}</td>
<td>1.189x10^{-1}</td>
<td>1.175x10^{-1}</td>
<td>1.153x10^{-1}</td>
</tr>
<tr>
<td>0.80</td>
<td>1.947x10^{-1}</td>
<td>1.487x10^{-1}</td>
<td>1.477x10^{-1}</td>
<td>1.468x10^{-1}</td>
<td>1.491x10^{-1}</td>
<td>1.424x10^{-1}</td>
</tr>
<tr>
<td>0.85</td>
<td>2.406x10^{-1}</td>
<td>1.851x10^{-1}</td>
<td>1.839x10^{-1}</td>
<td>1.829x10^{-1}</td>
<td>1.808x10^{-1}</td>
<td>1.776x10^{-1}</td>
</tr>
<tr>
<td>0.90</td>
<td>3.019x10^{-1}</td>
<td>2.348x10^{-1}</td>
<td>2.334x10^{-1}</td>
<td>2.322x10^{-1}</td>
<td>2.297x10^{-1}</td>
<td>2.258x10^{-1}</td>
</tr>
<tr>
<td>0.95</td>
<td>3.941x10^{-1}</td>
<td>3.119x10^{-1}</td>
<td>3.102x10^{-1}</td>
<td>3.086x10^{-1}</td>
<td>3.056x10^{-1}</td>
<td>3.009x10^{-1}</td>
</tr>
<tr>
<td>0.99</td>
<td>5.562x10^{-1}</td>
<td>4.512x10^{-1}</td>
<td>4.490x10^{-1}</td>
<td>4.471x10^{-1}</td>
<td>4.433x10^{-1}</td>
<td>4.373x10^{-1}</td>
</tr>
</tbody>
</table>
(Table 3 continued)

<table>
<thead>
<tr>
<th>Fractional attainment of equilibrium U(τ)</th>
<th>Dimensionless time, τ</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ = ( \frac{D_{OH}}{D_{CrO_4}} )</td>
<td>λ = ( \frac{D_{OH}}{D_{SO_3}} )</td>
</tr>
<tr>
<td>2.500</td>
<td>2.478</td>
</tr>
<tr>
<td>0.01</td>
<td>1.321×10^{-5}</td>
</tr>
<tr>
<td>0.05</td>
<td>3.308×10^{-4}</td>
</tr>
<tr>
<td>0.10</td>
<td>1.329×10^{-3}</td>
</tr>
<tr>
<td>0.15</td>
<td>3.013×10^{-3}</td>
</tr>
<tr>
<td>0.20</td>
<td>5.411×10^{-3}</td>
</tr>
<tr>
<td>0.25</td>
<td>8.571×10^{-3}</td>
</tr>
<tr>
<td>0.30</td>
<td>1.255×10^{-2}</td>
</tr>
<tr>
<td>0.35</td>
<td>1.744×10^{-2}</td>
</tr>
<tr>
<td>0.40</td>
<td>2.334×10^{-2}</td>
</tr>
<tr>
<td>0.45</td>
<td>3.040×10^{-2}</td>
</tr>
<tr>
<td>0.50</td>
<td>3.880×10^{-2}</td>
</tr>
<tr>
<td>0.55</td>
<td>4.879×10^{-2}</td>
</tr>
<tr>
<td>0.60</td>
<td>6.070×10^{-2}</td>
</tr>
<tr>
<td>0.65</td>
<td>7.499×10^{-2}</td>
</tr>
<tr>
<td>0.70</td>
<td>9.230×10^{-2}</td>
</tr>
<tr>
<td>0.75</td>
<td>1.136×10^{-1}</td>
</tr>
<tr>
<td>0.80</td>
<td>1.404×10^{-1}</td>
</tr>
<tr>
<td>0.85</td>
<td>1.791×10^{-1}</td>
</tr>
<tr>
<td>0.90</td>
<td>2.228×10^{-1}</td>
</tr>
<tr>
<td>0.95</td>
<td>2.973×10^{-1}</td>
</tr>
<tr>
<td>0.99</td>
<td>4.328×10^{-1}</td>
</tr>
<tr>
<td>Fractional attainment of equilibrium $U(\tau)$</td>
<td>Dimensionless time, $\tau$</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>$\lambda = \frac{D_{\text{HPO}<em>4}}{D</em>{\text{OH}}}$</td>
<td>$\lambda = \frac{D_{\text{SO}<em>4}}{D</em>{\text{OH}}}$</td>
</tr>
<tr>
<td>0.01</td>
<td>$4.982 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.05</td>
<td>$1.248 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.10</td>
<td>$5.027 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.15</td>
<td>$1.144 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.20</td>
<td>$2.068 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.25</td>
<td>$3.302 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.30</td>
<td>$4.886 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.35</td>
<td>$6.875 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.40</td>
<td>$9.341 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.45</td>
<td>$1.238 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.50</td>
<td>$1.614 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.55</td>
<td>$2.077 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.60</td>
<td>$2.648 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.65</td>
<td>$3.347 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.70</td>
<td>$4.332 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.75</td>
<td>$5.437 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.80</td>
<td>$6.915 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.85</td>
<td>$9.021 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.90</td>
<td>$1.236 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.95</td>
<td>$1.890 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.99</td>
<td>$3.327 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
(Table 4 continued)

<table>
<thead>
<tr>
<th>Fractional attainment of equilibrium $U(\Upsilon)$</th>
<th>Dimensionless time, $\Upsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_1 = \frac{D_{CrO_4}}{D_{OH}}$</td>
<td>$\lambda_2 = \frac{D_{SO_2}/SO_4}{D_{OH}}$</td>
</tr>
<tr>
<td>= 0.400</td>
<td>= 0.404</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>0.01</td>
<td>6.543x10^{-6}</td>
</tr>
<tr>
<td>0.05</td>
<td>1.638x10^{-4}</td>
</tr>
<tr>
<td>0.10</td>
<td>6.588x10^{-4}</td>
</tr>
<tr>
<td>0.15</td>
<td>1.496x10^{-3}</td>
</tr>
<tr>
<td>0.20</td>
<td>2.693x10^{-3}</td>
</tr>
<tr>
<td>0.25</td>
<td>4.279x10^{-3}</td>
</tr>
<tr>
<td>0.30</td>
<td>6.292x10^{-3}</td>
</tr>
<tr>
<td>0.35</td>
<td>8.784x10^{-3}</td>
</tr>
<tr>
<td>0.40</td>
<td>1.182x10^{-2}</td>
</tr>
<tr>
<td>0.45</td>
<td>1.551x10^{-2}</td>
</tr>
<tr>
<td>0.50</td>
<td>1.995x10^{-2}</td>
</tr>
<tr>
<td>0.55</td>
<td>2.532x10^{-2}</td>
</tr>
<tr>
<td>0.60</td>
<td>3.185x10^{-2}</td>
</tr>
<tr>
<td>0.65</td>
<td>3.982x10^{-2}</td>
</tr>
<tr>
<td>0.70</td>
<td>5.238x10^{-2}</td>
</tr>
<tr>
<td>0.75</td>
<td>6.536x10^{-2}</td>
</tr>
<tr>
<td>0.80</td>
<td>8.238x10^{-2}</td>
</tr>
<tr>
<td>0.85</td>
<td>1.060x10^{-1}</td>
</tr>
<tr>
<td>0.90</td>
<td>1.416x10^{-1}</td>
</tr>
<tr>
<td>0.95</td>
<td>2.053x10^{-1}</td>
</tr>
<tr>
<td>0.99</td>
<td>3.569x10^{-1}</td>
</tr>
</tbody>
</table>