**Diffusion mechanism of cesium, cobalt and cadmium ions in the particles of tin vanadate as a cation exchanger**

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The mechanism of diffusion of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) ions in the H-form of tin-vanadate as cation exchanger was studied as a function of particle size, concentration of the exchanging ions, reaction temperature, and drying temperature. The exchange rate was controlled by a particle diffusion mechanism as a limited batch technique and is confirmed from straight lines of $B$ versus $1/r^2$ plots. The values of diffusion coefficients, activation energy, and entropy of activation were calculated and their significance was discussed. The data obtained were compared with those reported for other inorganic ion exchangers.

**Key words:** Diffusion mechanism, cesium, cobalt, cadmium, tin vanadate, cation exchanger.

**INTRODUCTION**

A good deal of interest has grown in the last decades in synthetic inorganic ion exchangers (Zakaria et al., 2003), because of their greater resistance to high radiation doses and highly elevated temperatures which is of a great importance in the nuclear technology (Marinsky and Marcus, 1995). There has been an increasing interest in studying the kinetics and equilibrium characteristics of inorganic ion exchangers (Grebenyuk et al., 1998; Varshney et al., 2000; Rawat and Khan, 1980).

Kinetic studies of H-metal ion exchanges on ion exchange materials are important for their analytical applications, since the kinetic studies of a reaction allow us to understand the mechanism, rate determining step, and rate laws obeyed by a diffusion process. Energy of activation, entropy of activation, and the self-diffusion coefficient of the ions ($E_a$, $\Delta S^*$, and $D_i$) are the fundamental properties of a system. These parameters help us to understand the mechanism of reactions during adsorption/ exchange process. Hence, it is important to deal with the kinetic behavior of the material for the exchange of various metal ions (El-Naggar et al., 2007). Some studies on the kinetics of ion exchange on synthetic zirconium phosphate (Clearfield et al., 1970) and titanium oxide (Ghoneimy, 1999) have been reported. The few studies on vanadates on ion-exchangers have been summarized recently on nano-zirconium vanadate (Abd El-Latif and Elkady, 2011), zirconium vanadate and ceric vanadate (Lahiri et al., 2005), zirconium vanadate (Roy et al., 2002) and Tin(IV) vanadate (Qureshi et al., 1976). In the course of the successful application of these ion exchange materials, our interest has been directed to study the diffusion mechanism of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) on the prepared tin-vanadate (SnV) under the control of particle diffusion mechanism. Some aspects on SnV: SnV is a yellow colour material in the form of granules, from X-Ray fluorescence (XRF) studies, it is clear that, it contains 55.89% SnO\(_2\), 33.81% V\(_2\)O\(_5\), and 9.6% H\(_2\)O. From X-Ray diffraction (XRD), it is clear that SnV has amorphous structure, and after heating SnV at 600°C, SnV shows less significant change in the structure (it becomes semi crystalline).

**MATERIALS AND METHODS**

All chemical used were of analytical reagent grade purity and were
used without further purification.

**Preparation of SnV**

SnV can be synthesized by the addition of equimolar amount of stannic tetra chloride (SnCl₄) and sodium monovanadate (NaVO₃) as the following 0.5 M stannic tetrachloride was dissolved in 4 M hydrochloric acid, and then was added to 0.5 M sodium monovanadate in a volume ratio of 1:1 with constant stirring at room temperature. After the addition was completed, ammonia was added until a precipitation occurred and then the reaction mixture was allowed to settle for 24 h. The precipitate was filtered, washed several times with deionized water. The precipitate was dried at 50°C in an electric oven, ground and sieved for different mesh sizes, and was stored at room temperature.

**Kinetics studies**

The radius of the particles of the sieved fractions was determined by measuring the diameter of 100 particles with an optical microscope. The particles were assumed to be spherical and a mean equivalent radius was calculated. The reaction takes place between the metal ions and the counter ions in the exchanger, and the rates are controlled by a particle diffusion mechanism only. Kinetics experiments were performed by using batch factor of V/m equals 100 ml/g and 10⁻² M metal chloride solution in a shaker thermostat adjusted at the desired temperatures. After the adjusted interval period, the solid was separated immediately from the solution and the extent of sorption was determined as the following:

\[
F(t) = \frac{Q_f}{Q_e} = \frac{\text{Amount of exchange after time, } t}{\text{Amount of exchange after infinite time}}
\]

for the particle diffusion controlled kinetics, the expression developed by Boyed et al. (1947) and improved by Reichenberg(1953) is as shown in Equation 1, which is used in this work:

\[
F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2Bt}
\]

and

\[
B = \frac{\pi^2 D_i}{r^2}
\]

where B is a mathematical function, D_i is the diffusion coefficient of the ions undergoing exchange within the exchanger, n is an integer number, and r refers to the radius of the particles. When F(t) is less than 0.4, Equation 1 can be approximated in a simpler form:

\[
F(t) = \frac{6}{\pi} \left( \frac{D_i t}{\pi} \right)^{1/2}
\]

which hold to a fairly good approximation. Therefore, a plot of F(t) against the square root of the contact time must be give a straight line passing through the origin in which F(t) is less than 0.4.

**RESULTS**

The result of this study showed that tin vanadate is a brown colour material in the form of granules. From XRD studies it was clear that it contains 55.89% SnO₂, 33.81% V₂O₅, and 9.3% H₂O. From XRD studies it was also clear that it is an amorphous material but by increasing the heating temperature its crystallinity was improved.

**DISCUSSION**

**Mathematical model**

The experimental conditions of the present study were set for the particle diffusion mechanism only (as mentioned earlier). The fractional attainment of equilibrium at time t, F(t), was used and is expressed as:

\[
A_i - A_f
\]

where A_i and A_f are the initial and final concentrations (ppm) of the metal ions in solution.

**Analysis**

The metal ions (Cs⁺, Co²⁺, and Cd²⁺) investigated in this work were analyzed by atomic absorption. The diffused ions (Cs⁺, Co²⁺, and Cd²⁺) are used in this work by concentration (10⁻³ M) of each ion in case of reaction temperature, drying temperature, and particle diameters effect studies, but in case of the study of effect of concentration, these ions were used in concentrations: 10⁻³, 5 × 10⁻³, 10⁻² M, and these concentrations can be converted to ppm concentration by the following equation.

\[
M = \frac{\text{ppm} \times 10^3}{\text{Atomic weight of element}}
\]

All tests were repeated two or three times and the experimental error was about ±3%, the results agreed that, the reproducibility of measurements was more than 98%.
Table 1. Values of the diffusion coefficient of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) on different particle diameters of tin vanadate at 25 ± 1°C.

<table>
<thead>
<tr>
<th>Particle diameter (± 0.02 mm)</th>
<th>D(_{i}) (×10(^9) cm(^2)s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.115</td>
<td>2.178</td>
</tr>
<tr>
<td>0.185</td>
<td>2.050</td>
</tr>
<tr>
<td>0.375</td>
<td>1.907</td>
</tr>
</tbody>
</table>

Table 2. Thermodynamic parameters of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}/H^+\) systems on SnV at different reaction temperatures.

<table>
<thead>
<tr>
<th>Exchange system</th>
<th>Drying temperature</th>
<th>Particle diameter (mm)</th>
<th>Reaction temperature (K)</th>
<th>D(_{i}) × 10(^9) cm(^2)s(^{-1})</th>
<th>D(_{o}) × 10(^7) cm(^2)s(^{-1})</th>
<th>E(_a) (kJmol(^{-1}))</th>
<th>∆S(^*) (Jmol(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(^+)/H(^+)</td>
<td>50°C</td>
<td>0.185 ± 0.02 mm</td>
<td>298</td>
<td>5.16</td>
<td>1.908</td>
<td>-121.48</td>
<td>-117.1</td>
</tr>
<tr>
<td>Co(^{2+}/H^+)</td>
<td></td>
<td></td>
<td>318</td>
<td>5.55</td>
<td>1.89</td>
<td>3.39</td>
<td>-121.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>338</td>
<td>6</td>
<td>1.907</td>
<td></td>
<td>-122.51</td>
</tr>
<tr>
<td>Cd(^{2+}/H^+)</td>
<td></td>
<td></td>
<td>298</td>
<td>4.37</td>
<td>2.106</td>
<td>-120.65</td>
<td>-116.66</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>318</td>
<td>4.92</td>
<td>2.15</td>
<td>3.984</td>
<td>-121.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>338</td>
<td>5.62</td>
<td>2.24</td>
<td></td>
<td>-121.16</td>
</tr>
</tbody>
</table>

Experimental conditions were chosen for particle diffusion mechanism as a main rate determining step (as a limited batch technique). The energy of activation (E\(_a\)) for the self-diffusion of cations was determined by applying the Arrhenius equation:

\[
D_i = D_o \ e^{-\frac{E_a}{RT}}
\]

(4)

where D\(_o\) is the self-diffusion coefficient. The entropy of activation (∆S\(^*\)) can be calculated from D\(_o\) by substitution in the equation proposed by Barrer et al. (1963):

\[
D_o = 2.72 \left( \frac{KTd^2}{h} \right) e^{\frac{\Delta S^*}{R}}
\]

(5)

where K is the Boltzmann constant, T is the absolute temperature, d is the average distance between two successive positions in the process of diffusion which was taken as 0.5 mm and h is the plank’s constant.

The aforementioned equations were used for calculating the values of D\(_o\), D\(_i\), E\(_a\), and ∆S\(^*\) for the exchanged systems and the obtained results are given in Tables 1 and 2.

Analysis of data

To verify the particle diffusion mechanism of the metal ions Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) on SnV (Tin vanadate) under the conditions set in the present work, the following experimental results were obtained: (1) the rate of exchange of different metal ions on SnV is independent on metal concentrations in solution up to 10\(^{-3}\) M, (2) straight line relationships passing through the origin were obtained between the function Bt and t for the three metal ions under study, (3) the exchange rate of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) were found to increase with the decrease of the particle size of the prepared SnV exchanger, and (5) the plots of B [the slopes of straight lines (Bt versus t plots)] versus 1/r\(^2\) for Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) on SnV gave straight lines. All these results provide a good base supporting the particle diffusion mechanism under our experimental conditions. Similar findings were previously reported (El-Naggar et al., 1999, 1992a; El-Naggar and Aly, 1992; El-Naggar and Absy, 1992; Mishra et al., 1996; Abou-Mesalam and El-Naggar, 2003b).

A study of the concentration effect on the rate of exchange for Cd\(^{2+}/H^+\) exchange at 25 ± 1°C shows that at concentration >10\(^{-3}\) M, the initial rate of exchange is independent of concentration as shown in Figure 1. The experimental conditions were set for particle diffusion mechanism only (Inczedy, 1996). The values of Bt at different time intervals for the exchange of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) ions on three different particle sizes of SnV were plotted as represented in Figures 2 to 4, respectively. Figures 2 to 4 show that the plots of Bt versus t for Cs\(^+\)/H\(^+\), Co\(^{2+}/H^+\), and Cd\(^{2+}/H^+\) systems are linear and start from the origin proving a particle diffusion control.
mechanism (Amphlett, 1964). Also, these figures indicate that the rate of exchange increases with decrease in the particle sizes, which agrees with the fundamental conditions of particle diffusion. The average values of diffusion coefficients ($D_i$) of Cs$^+$, Co$^{2+}$, and Cd$^{2+}$ on SnV of different particle diameters were calculated from the relations of $B_t$ versus $t$ (Figures 2 to 4 and Table 1). From this table it is found that the values of diffusion coefficient ($D_i$) which generally slightly increase with increase in the particle diameters of the prepared samples. The rate of exchange of Cs$^+$, Co$^{2+}$, and Cd$^{2+}$ ions on SnV increase
with decrease in the particle diameter which agree with the fundamental conditions of particle diffusion, which support the particle diffusion mechanism. This trend was also reported for others ion-exchangers (El-Naggar and Aly, 1992; El-Naggar and Absy, 1992). The higher values obtained of $D_i$ may be attributed to the large particles formed from agglomeration of smaller compact unites. Therefore, a quicker diffusion took place through the channels between these unites.

Furthermore, the self diffusion coefficients of the metal ions studied are independent on the metal ion concentration in solution and dependent on the particle size of the exchangers. This indicates that under these conditions, the rate determining step is mainly diffusion through the particle and film diffusion is nearly neglected and hence the mechanism of diffusion of these ions in our matrix is considered to be unchanged by the composition of the matrix (El-Naggar et al., 2010).

Plots of $B$ versus $1/r^2$ are straight lines indicating that the rate of exchange is inversely proportional to the square of the radius of the particle as shown in Figure 5, which again verifies that diffusion through the exchanger particle is the rate-determining step. The relations between $B_t$ and $F$ against time for the exchange of $\text{Cs}^+$, $\text{Co}^{2+}$, and $\text{Cd}^{2+}$ ions for a particle diameter $0.185 \pm 0.02$ mm and reaction temperatures 25, 45, and 65°C on SnV are as shown in Figures 6 to 8, respectively.

These relations gave straight lines passing through the origin in all studied cases. Found from these results, it was found out that the rate of exchange reaction increased with increase in the reaction temperature from 25 to 65 ± 1°C (El-Naggar et al., 1998). This trend may be due to the increase of the mobility of ions with increase in the reaction temperature from 25 to 65 ±1°C. This agrees with the reported results for the rate of exchange of $\text{Na}^+$ and $\text{Co}^{2+}$ on crystalline and amorphous sodium titanate at different reaction temperature (Zakaria et al., 2004).

The diffusion coefficient values ($D_i$) of the investigated metal ions were calculated from the slopes of the previous relations at 25, 45 and 65±1°C using Equation 1. The results are summarized in Table 2. From this table, it is clear that the values of diffusion coefficient of the investigated metal ions increase in the order: $\text{Cs}^+ > \text{Cd}^{2+} > \text{Co}^{2+}$. This trend could be attributed to the hydration energy and the hydrated ionic radii of the studied metal ions which take the order: $\text{Cs}^+ > \text{Cd}^{2+} > \text{Co}^{2+}$. Therefore, the mobility of these metal ions in the exchange particles increases in the reverse order (El-Naggar et al., 2007).

The effect of drying temperature of SnV (50, 200, and 400°C) on the rate of exchange of the investigated metal ions was studied as a relation between $F$ and $B_t$ against time as shown in Figures 9 to 11. From these figures, it was found out that the rate of exchange decreases by $\text{Cs}^+$, $\text{Co}^{2+}$, and $\text{Cd}^{2+}$ with an increase in the drying temperature of SnV from 50 to 400°C as shown in Table 3. The lowering in the $D_i$ values for $\text{Cs}^+$, $\text{Co}^{2+}$, and $\text{Cd}^{2+}$ with increase in the drying temperatures of the ion increasing the drying temperature from 50 to 400°C. It is clear that an appreciable decrease of self-diffusion of
exchanger from 50 to 400°C may be attributed to the decrease in the surface area and porosity of the dried exchanger as experimentally found (El-Naggar et al., 2007). The lower porosity means less free water inside the exchanger particles which hinders the diffusion of the metal ions (Misak and El-Naggar, 1989). When log $D_i$ is plotted against $1/T$ for the exchange of Cs$^+$, Co$^{2+}$, and Cd$^{2+}$ on SnV, straight lines were obtained (Figure 12).
The exchange kinetics of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) on the investigated metal ions (at 25°C) has the order: Cd\(^{2+}\)/H\(^+\) (4.91) > Co\(^{2+}\)/H\(^+\) (3.894) > Cs\(^+\)/H\(^+\) (3.239). This trend agrees with that already reported for Cs\(^+\) and Co\(^{2+}\) on SiTi (El-Naggar et al., 2007) which has the order: Co\(^{2+}\)/H\(^+\) (12.9) > Cs\(^+\)/H\(^+\) (11.87). The relatively small activation energy values (E\(_a\)) (kJ mol\(^{-1}\)) obtained (Table 2) for Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) indicated the rate of exchange of particle diffusion (El-Naggar et al., 1992a).

It is interesting to compare the values of activation energies which have been observed for all studied metal ions reported in Table 2 with other values of activation energies which have been observed for the exchange of other metal ions on polypyrrole/polyantimonic acid and acrylamide cerium(IV) phosphate, whereas the activation energy values have been observed for the exchange of other inorganic ion exchangers which confirm the particle diffusion mechanism.

The negative \(\Delta S^*\) values obtained for all studied systems are given in Table 2. The negative values obtained for the entropy of activation, suggest that no significant structure change occur in SnV. The entropy change normally depends on the extent of hydration of the exchangeable and exchanging ions a long with any change in water structure around ions that may occur when they pass through the channels of exchanger particles. The lowest values of \(\Delta S^*\) for Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) on SnV support the higher stability and hence the least steric difference of the system. These results are parallel to that reported for other inorganic exchanger (El-Naggar et al., 1992b).

The activation energy was found to decrease with the decrease in the entropy of the activation of the system (Table 2). The same trend was observed for other ion exchange materials (Abou-Mesalam and El-Naggar, 2003b).

**Conclusion**

The exchange kinetics of Cs\(^+\), Co\(^{2+}\), and Cd\(^{2+}\) on the
prepared SnV were studied as a function of concentration, particle radius, drying temperature of SnV and reaction temperatures. The rate of exchange is independent on the metal ion concentration and this is considered as an evidence for the particle diffusion mechanism for all investigated metal ions. The rate of exchange increases with decrease in the particle size and drying the temperature of the exchange materials. While, the rate increases with increasing the reaction temperature. The diffusion coefficient values (D) of Cs\(^{2+}\), Co\(^{2+}\), and Cd\(^{2+}\) ions on SnV are decreased with increase in the drying temperatures from 50 to 400°C and this indicates that the diffusion ion (Cs\(^{2+}\), Co\(^{2+}\), and Cd\(^{2+}\)) are diffused in the dehydrated form. Negative values of entropy of activation (ΔS\(^{v}\)) were obtained and this anticipate that the investigated metal ions are exchange with H\(^{+}\) of SnV in the unhydrated form.

**REFERENCES**


Table 3. Values of diffusion coefficient of Cs\(^{2+}\), Co\(^{2+}\) and Cd\(^{2+}\) on SnV at different drying temperature and at particle diameter 0.185 ± 0.02 mm.

<table>
<thead>
<tr>
<th>Exchange system</th>
<th>Drying temperature (°C)</th>
<th>Di x 10^9 cm^2 s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(^{+})/H(^{+})</td>
<td>50</td>
<td>1.564</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4.567</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>3.619</td>
</tr>
<tr>
<td>Co(^{2+})/H(^{+})</td>
<td>50</td>
<td>4.373</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.71</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>3.36</td>
</tr>
<tr>
<td>Cd(^{2+})/H(^{+})</td>
<td>50</td>
<td>4.68</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4.02</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>3.602</td>
</tr>
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