Kinetic Studies of some Hazardous Metal Ions in the Particle of Titanium Potassium Vanadate as a Cation Exchanger

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ABSTRACT

Titanium potassium vanadate (TiKV) as an inorganic ion exchange material was synthesized from titanium tetrachloride, potassium chloride and sodium monovanadate with molar ratio Ti:K:V=1:1:1. The kinetic behaviour of Cs⁺, Co²⁺ and Cd²⁺ have been studied under different conditions of concentration, particle size, reaction temperatures and drying temperatures. The experimental conditions were set to favour particle diffusion control. The values of diffusion coefficient (D_i), activation energy (E_a), entropy of activation (S*), enthalpy change (H*) and free energy change (G*) were calculated and their significance was discussed. The data obtained have been compared with those reported for other inorganic ion exchangers.

Key Words: Diffusion / Ion Exchange / Titanium Potassium Vanadate / Thermodynamic Parameters.

1-INTRODUCTION

During the last 2 decades much attention has been paid to the development of inorganic ion exchange materials with high selectivities and higher resistance to temperatures and radiation than those of commercial resins [1].

A study of kinetics of ion exchange enables us to understand the viability of an exchange material in separation technology. Earlier, the old Bt criterion [2] was used for such a study [3], which is best for an isotope-exchange process [4] in which ions have similar effective diffusion coefficients. However, for a true ion exchange process involving metal ions of different diffusion coefficients, the new approach based on Nernst-Plank equations [5-7] should be more relevant.

The study of the kinetics on titanium potassium vanadate is important since it provides information on the reactions accompanying the ion exchange as well as on the internal physical structure of the exchanger and the extent of hydration of the exchanging ions [8]. The present work reports the kinetics and thermodynamics of exchange of Cs⁺, Co²⁺ and Cd²⁺ ions on synthesized titanium potassium vanadate ion exchanger. Experimental and theoretical aspects are done to show that the rate determining step is diffusion through the particles of titanium potassium vanadate (TiKV). The diffusion coefficients (D_i), activation energies (E_a), enthalpy change (?H*), entropies and free energies of activation (?S* and ?G*) have been calculated for Cs⁺, Co²⁺ and Cd²⁺ ions in aqueous solution.

2-EXPERIMENTAL

2.1. Chemical reagents and instruments:

The main reagents used for the synthesis of the material were obtained from BDH (England) and Loba Chemie (India). All reagents and chemicals were of analytical reagent grade purity and used without further purification. All measurements were performed using an atomic absorption spectrophotometer model AA-6701F – Shimadzu, Kyoto "Japan".

2.2. Preparation of titanium potassium vanadate (TiKV):

0.5M titanium tetrachloride was dissolved in 4M hydrochloric acid then was added to a mixture of [0.5M sodium monovanadate and 0.5M potassium chloride] with a volume ratio Ti:K:V=
1:1:1 with constant stirring at room temperature. After the addition was completed, ammonia was added until a precipitation was occurred and then the reaction mixture was allowed to settle for 24 hours. The precipitate was filtered, washed several times with deionized water. The precipitate was dried at 50°C in an electric oven, grained and sieved for different mesh sizes and stored at room temperature.

2.3. Kinetic Studies:

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Cs⁺, Co²⁺ and Cd²⁺ on TiKV. The particle diffusion-controlled phenomenon is favored by a high metal ion concentration, a relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture.

The particle size of the solid was evaluated by an optical microscope. The particles are assumed to be spherical and a mean equivalent was calculated.

The kinetic measurements were carried out at different concentrations of metal ions (10⁻² M, 5x10⁻³ M and 10⁻³ M) and different particle diameters (0.375, 0.185, 0.115±0.02 mm) of TiKV with V/m equals 100 mlg⁻¹. This was performed using an aqueous solution contains the metal cations. All kinetic experiments were done in a shaker thermostat adjusted at the desired temperatures (25, 45 and 65±1°C). After each interval time the shaker was stopped and the solution was separated immediately from the solid and the extent of sorption was determined, as follows

\[
\% \text{ sorption} = \left( \frac{(A_i - A_f)}{A_i} \right) \times 100
\]

where Aᵢ and Aₐ are the initial and final concentration of the metal ions in solution.

2.4. Analysis:

The metal ions (Cs⁺, Co²⁺ and Cd²⁺) investigated in this work were analyzed by atomic absorption. 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%.

3-RESULTS &DISCUSSION

The rate controlling step in ion exchange is usually either liquid film diffusion or particle diffusion [9]. The equations developed by Boyed et al.,[10] and improved by Reichenberg [3] were used for evaluating the kinetics parameters, then the following equations were used;

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

and

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

where, F is the fractional attainment at equilibrium, n is an integer number, B is a mathematical function, Dᵢ is the diffusion coefficient of the ions (Cm²/s) and r is the radius of the particles (Cm).

When the fraction attainment of equilibrium F is less than 0.4, the above equation (Eq.1) can be approximated to a simpler form as follows;

\[
F = 6 \left( \frac{D_i t}{\pi r^2} \right)^{1/3}
\]

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

The study of the effect of concentration on the rate of exchange of Cd²⁺ ion on TiKV at 25±1°C and 0.185±0.02 mm mesh size showed at concentrations (5x10⁻³, 10⁻³ and 5x10⁻³M). From the data presented in Fig.(1), at the concentrations studied, the rate of exchange is independent of the
metal ion concentration. So, this is the evident that the concentrations condition set in this paper are particle diffusion mechanism for all metal ions studied and the film diffusion can be excluded at this concentration condition $5 \times 10^{-3}$ M (generally used in this work). Similar findings were previously reported [11-14].

![Graph showing plots of F against time for the exchange of different concentrations of Cd$^{2+}$ on TiKV at 25±1ºC.](image)

Fig.(1): Plots of F against time for the exchange of different concentrations of Cd$^{2+}$ on TiKV at 25±1ºC.

The effect of particle size of TiKV on the rate of exchange of Cs$^+$, Co$^{2+}$ and Cd$^{2+}$ at 25±1ºC are represented in Fig.(2) in terms of Bt vs. t plots. It was found that straight lines passing through the origin in all cases are obtained, and the rate of exchange of Cs$^+$, Co$^{2+}$ and Cd$^{2+}$. Our results agree with that reported before [15, 16] for other ion exchangers.

![Graphs showing plots of F and Bt against time for the exchange of Cs$^+$, Co$^{2+}$ and Cd$^{2+}$ ions on different particle diameters of TiKV at 25±1ºC.](images)

Fig.(2): Plots of F and Bt against time for the exchange of Cs$^+$, Co$^{2+}$ and Cd$^{2+}$ ions on different particle diameters of TiKV at 25±1ºC.
Table (1) shows the averages values of diffusion ($D_i$) for the investigated metal ions at different particle diameters which are calculated from the relations of $B_t$ vs; Fig.(2). It was found that the effective diffusion coefficient values ($D_i$) are slightly increase with increasing the particle diameters of the prepared ion exchanger. This difference was also observed by others [16, 25] who assumed that large particles are formed from agglomerated small particle units and, therefore, a quicker diffusion took place through the channels between these units [16].

The rate of exchange of $\text{Cs}^+$, $\text{Co}^{2+}$ and $\text{Cd}^{2+}$ ions on TiKV increases with decreasing the particle diameter which agrees with the fundamental conditions of particle diffusion, which support the particle diffusion mechanism. This trend was reported for others ion exchangers [15, 17].

**Table (1): values of the diffusion coefficient of $\text{Cs}^+$, $\text{Co}^{2+}$ and $\text{Cd}^{2+}$ ions on different particle diameters of TiKV at 25±1ºC.**

<table>
<thead>
<tr>
<th>Particle diameters (±0.02 mm)</th>
<th>$\text{Cs}^+$ ($\text{cm}^2\text{s}^{-1}$)</th>
<th>$\text{Co}^{2+}$ ($\text{cm}^2\text{s}^{-1}$)</th>
<th>$\text{Cd}^{2+}$ ($\text{cm}^2\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.115</td>
<td>2.58 x10^{-9}</td>
<td>2.26 x10^{-9}</td>
<td>2.956 x10^{-9}</td>
</tr>
<tr>
<td>0.185</td>
<td>5.65 x10^{-9}</td>
<td>5.51 x10^{-9}</td>
<td>6.6 x10^{-9}</td>
</tr>
<tr>
<td>0.375</td>
<td>0.191 x10^{-9}</td>
<td>0.202 x10^{-9}</td>
<td>0.198 x10^{-9}</td>
</tr>
</tbody>
</table>

The highly values obtained for $D_i$ may be attributed to the large particles formed from agglomerated of smaller compact unites. Therefore, a quicker diffusion took place through the channels between these unites [16, 25]. Furthermore, the diffusion coefficients of the metal ions studied are independent of the metal ion concentration in solution and dependent on the particle size of exchangers. This indicates that under these conditions, the rate determining step is mainly diffusion through the particle and the 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 [18].

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 particles as shown in Fig.(3). Which again verifies that diffusion through the exchanger particle is the rate-determining step.

![Fig.(3): Plots of B against 1/r^2 for the exchange of $\text{Cs}^+$, $\text{Co}^{2+}$ and $\text{Cd}^{2+}$ on TiKV at 25±1ºC.](chart.png)
The effect of varying reaction temperatures (25, 45 and 65±1°C) on the rate of exchange of Cs⁺, Co²⁺ and Cd²⁺ ions was investigated on TiKV as a relation between F and Bt against contact time [Fig.(4)]. It was found that the relation between Bt vs. t gives straight lines passing through the origin in all cases. Furthermore, it is seen from these figures that the rate of exchange reaction of Cs⁺, Co²⁺ and Cd²⁺ on TiKV increases with increasing the reaction temperature from 25 to 65 ±1°C.

Fig.(4): Plots of F and Bt against time for the exchange of Cs⁺, Co²⁺ and Cd²⁺ on TiKV at different reaction temperatures.

This trend may be due to increasing the mobility of ions with increasing the reaction temperature from 25 to 65±1°C. Similar findings were obtained for the exchange of Rb²⁺ and Cs⁺ on zirconium antimonate [19] also for the exchange of Pb²⁺, Cd²⁺ and Zn²⁺ ions on antimonic acid [18].

The values of diffusion coefficient (Dᵢ) were calculated for Cs⁺, Co²⁺ and Cd²⁺ on TiKV and given in Table (3). From this table it is clear that the values of diffusion coefficient of the investigated metal ions increase in the order:

\[ \text{Cd}^{2+} > \text{Cs}^{+} > \text{Co}^{2+} \]

This trend could attributed to the ionic radii of the exchanged ions which take the order (Cd < Cs). This ion with smaller ionic radius is easily exchanged and moves faster than that the ion with greater ionic radii, the lower Dᵢ value of Cd²⁺ may be due to the higher hydration energy of Cd²⁺ ion as seen in Table (2).

**Table (2): Ionic radii and hydration energy of exchange systems.**

<table>
<thead>
<tr>
<th>Exchange system</th>
<th>Ionic radii</th>
<th>Hydration energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd²⁺ /H⁺</td>
<td>0.97</td>
<td>1806</td>
</tr>
<tr>
<td>Cs²⁺ /H⁺</td>
<td>1.67</td>
<td>263</td>
</tr>
<tr>
<td>Co²⁺ /H⁺</td>
<td>0.72</td>
<td>2034</td>
</tr>
</tbody>
</table>
Table (3): Thermodynamic parameters of Cs$^+$, Co$^{2+}$ and Cd$^{2+}$/H$^+$ systems on TiKV at different reaction temperatures.

<table>
<thead>
<tr>
<th>Exchange system</th>
<th>Drying temperature</th>
<th>Particle diameter, mm.</th>
<th>Reaction Temp., °C</th>
<th>$D_i$ (cm$^2$s$^{-1}$ x10$^8$)</th>
<th>$D_o$ (cm$^2$s$^{-1}$ x10$^8$)</th>
<th>$E_a$ kJmol$^{-1}$</th>
<th>$\Delta S^*$ Jmol$^{-1}$ k$^{-1}$</th>
<th>$\Delta H^*$ Jmol$^{-1}$ k$^{-1}$</th>
<th>$\Delta G^*$ Jmol$^{-1}$ k$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$^+/H^+$</td>
<td>50°C</td>
<td>0.185 ±0.02mm</td>
<td>298</td>
<td>5.65</td>
<td>7.25</td>
<td>6.319</td>
<td>-110.35</td>
<td>90.37</td>
<td>123.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>318</td>
<td>6.59</td>
<td>7.19</td>
<td>-110.98</td>
<td>87.22</td>
<td>122.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>338</td>
<td>7.38</td>
<td>7.02</td>
<td>-111.69</td>
<td>84.32</td>
<td>122.08</td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}/H^+$</td>
<td></td>
<td></td>
<td>298</td>
<td>5.51</td>
<td>2.01</td>
<td>3.167</td>
<td>-120.99</td>
<td>87.26</td>
<td>123.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>318</td>
<td>5.85</td>
<td>1.95</td>
<td>-121.84</td>
<td>84.73</td>
<td>123.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>338</td>
<td>6.40</td>
<td>1.99</td>
<td>-122.15</td>
<td>81.94</td>
<td>123.23</td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}/H^+$</td>
<td></td>
<td></td>
<td>298</td>
<td>6.60</td>
<td>2.82</td>
<td>3.599</td>
<td>-118.22</td>
<td>86.75</td>
<td>121.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>318</td>
<td>6.85</td>
<td>2.69</td>
<td></td>
<td>-119.14</td>
<td>84.25</td>
<td>122.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>338</td>
<td>7.76</td>
<td>2.79</td>
<td></td>
<td>-119.36</td>
<td>81.34</td>
<td>121.69</td>
</tr>
</tbody>
</table>

The effect of drying temperature of TiKV (50, 200 and 400±1°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 Fig.(5).

![Fig.5](image_url)

Fig.(5): Plots of $F$ and $B_t$ against time for the exchange of Cs$^+$, Co$^{2+}$ and Cd$^{2+}$ on TiKV at different drying temperature.

From these figures it is found that the rate of exchange decreases by increasing the drying temperature from 50 to 400±1°C. It is clear that an appreciable decrease of $D_i$ of Cs$^+$, Co$^{2+}$ and Cd$^{2+}$ with an increase in the drying temperature TiKV from 50 to 400±1°C as shown in Table (4).
Table (4): Values of diffusion coefficient of Cs⁺, Co²⁺ and Cd²⁺ on TiKV at different drying temperature and at particle diameter 0.185±0.02 mm.

<table>
<thead>
<tr>
<th>Exchange system</th>
<th>Drying temperature</th>
<th>Dᵢ (cm² s⁻¹ x10⁹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs⁺/H⁺</td>
<td>50°C</td>
<td>5.65</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>4.74</td>
</tr>
<tr>
<td></td>
<td>400°C</td>
<td>4.06</td>
</tr>
<tr>
<td>Co²⁺/H⁺</td>
<td>50°C</td>
<td>5.51</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td>400°C</td>
<td>4.39</td>
</tr>
<tr>
<td>Cd²⁺/H⁺</td>
<td>50°C</td>
<td>6.60</td>
</tr>
<tr>
<td></td>
<td>200°C</td>
<td>5.66</td>
</tr>
<tr>
<td></td>
<td>400°C</td>
<td>4.93</td>
</tr>
</tbody>
</table>

The lowering in the Dᵢ values for Cs⁺, Co²⁺ and Cd²⁺ ions with increasing the drying temperature of the TiKV from 50 to 400±1°C may be attributed to the lower pore sizes and porosity for the dried exchanger [20, 21]. The lower porosity means less free water inside the exchanger particles which hinders the diffusion of ions [22].

When log Dᵢ is plotted against 1/T for the exchange of Cs⁺, Co²⁺ and Cd²⁺ ions on TiKV (Fig. 6), straight lines were obtained (Fig. 6). From the slope of these lines and applying Arrhenius equation, Eq.(4). The energy of activation (Eₐ) and the diffusion coefficient (Dᵢ) were calculated.

\[ Dᵢ = Dₒ \exp \left( \frac{-Eₐ}{RT} \right) \]  \hspace{1cm} (4)

where Dₒ is the self-diffusion coefficient, Eₐ is the activation energy, R is the gass constant and T is the absolute temperature (t + 273K).

The activation energies (Eₐ) of Cs⁺, Co²⁺ and Cd²⁺ ions are calculated and tabulated in table (3). Table (3) shows that Co²⁺ has a lower activation energy which reflect the ease with which Co²⁺ ion can pass through the particles of TiKV compared to other cations (Cs⁺ and Cd²⁺). The relatively small activation energies values, (Eₐ) obtained table (3) for Cs⁺, Co²⁺ and Cd²⁺ on TiKV, indicated that the rate of exchange is particle diffusion [26].

![Fig.(6): Arrhenius plots for exchange of Cs⁺, Co²⁺ and Cd²⁺ on TiKV at different reaction temperature.](image-url)
Calculation of $D_o$ from equation (4) and substitution in equation (5), the entropy of activation ($\Delta S^*$) can be calculated by using Borrer et al., equation [23];

$$D_o = (2.71 \times 10^{-2} KT/h) \exp^{\Delta S^*/R}$$  \hspace{1cm} (5)$$

where $d$ is the ionic jump distance assumed equal to 0.5 mm, $K$ is the Boltzmann constant, $h$ is the plank constant and $T$ is the absolute temperature ($^\circ K$).

The negative $\Delta S^*$ values obtained for all systems studied are given in table 2, the entropy change normally depends on the extent of hydration and the exchangeable and exchanging ions. The negative values obtained for the entropy of activation, suggest that no significant structural change occurs in TiKV, also, the lower values of $\Delta S^*$ for $Cs^+$, $Co^{2+}$ and $Cd^{2+}$ on TiKV support the higher stability and hence the less steric difference of the system. These results are parallel to those reported for other ion exchangers [2, 3], [16, 25].

The activation energy was found to decrease with the decrease in the entropy of the activation of the system (Table 3). The same trend was observed for other ion exchange materials [14]. The relationship between $E_a$ and $\Delta S^*$ values for the exchange of $Cs^+$, $Co^{2+}$ and $Cd^{2+}$ on titanium potassium vanadate (TiKV) at 25±1ºC gave a linear relationship (Fig. 7). This result indicate that the $E_a - \Delta S^*$ compensation mechanism holds for the ion exchange system on the TiKV. Therefore, the physico-chemical origin of the $E_a - \Delta S^*$ compensation is probably related to an intrinsic property of hydration. Thus, from the above results and the negative values of $\Delta S^*$ reported in table 2, it is anticipated that the $Cs^+$, $Co^{2+}$ and $Cd^{2+}$ ions exchange with $H^+$ into the exchanger is in the unhydrated form [12].

![Fig.(7): The correlation between $\Delta S^*$ and $E_a$ for $Cs^+$, $Co^{2+}$ and $Cd^{2+}$ on TiKV at 25±1ºC.](image)

The free energy of activation ($\Delta G^*$) has been calculated from the equation proposed by Barrer et al. [24].

$$D_i = (KTd^2/h) \exp^{[\Delta G^*/R]}$$  \hspace{1cm} (6)$$

and the values of enthalpy ($\Delta H^*$) can be calculated from the following relation;
\[ \Delta G^* = \Delta H^* - T \Delta S^* \]  

The values of \( D_i, D_o, E_a, \Delta S^*, \Delta G^* \) and \( \Delta H^* \) for the exchange of Cs\(^+\), Co\(^{2+}\) and Cd\(^{2+}\) ions on titanium potassium vanadate ion exchanger have been calculated and tabulated in table (3).

Also, the negative values of \( \Delta S^* \) suggests that upon exchange of these cations, no significant structural change occur in titanium potassium vanadate ion exchanger.

Additionally, the positive values of free energy (\( \Delta G^* \)) and enthalpy change (\( \Delta H^* \)) reported in Table (3) for the exchange of Cs\(^+\), Co\(^{2+}\) and Cd\(^{2+}\) ions on the particles of TiKV suggest that these reactions require energy to covert reactants into products and the overall exchange process is non-spontaneous and have endothermic nature.

4-CONCLUSIONS

- The exchange kinetics of Cs\(^+\), Co\(^{2+}\) and Cd\(^{2+}\) on the prepared Titanium Potassium Vanadate (TiKV) were studied as a function of concentration, particle radius, drying temperature of TiKV and reaction temperatures.
- The rate of exchange is independent on the metal ion concentration, and This is evident that the conditions set in this work to are, particle diffusion mechanism for all investigated metal ions.
- The rate of exchange increases with decreasing the particle size and drying temperature of the exchange materials. However, the rate increases with increasing the reaction temperature.
- The diffusion coefficient values (\( D_i \)) of Cs\(^+\), Co\(^{2+}\) and Cd\(^{2+}\) ions on TiKV at 25\(^\circ\)C decrease with increasing the drying temperatures from 50 to 400\(^\circ\)C.
- Negative values of entropy of activation (\( \Delta S^* \)) were obtained and this anticipate that the investigated metal ions are exchanged with H\(^+\) of TiKV in the unhydrated form.
- The positive values of free energy (\( \Delta G^* \)) and enthalpy change (\( \Delta H^* \)) were obtained and suggest that these reactions require energy to covert reactants into products and the overall exchange process is non-spontaneous and have endothermic nature.

5-REFERENCES