Ion-exchange kinetics on styrene supported zirconium(IV) tungstophosphate: An organic-inorganic type cation exchanger

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Received 25 November 2000; revised received 15 January 2002; accepted 19 March 2002

Styrene supported zirconium(IV) tungstophosphate (SZWP) is a new organic-inorganic type ion-exchange material which has been synthesized1, showing excellent ion exchange properties. The kinetics of the surface phenomenon occurring on these materials is of great importance in understanding the mechanism of ion-exchange process. Although a large number of kinetic studies on such materials have been reported2-7, earlier approaches were based on the Bt criterion8, which is applicable only for an isotopic exchange process. In a true ion-exchange process where the fluxes of two different ionic species are coupled with one another9, a single diffusion coefficient cannot describe the actual process. A new approach based on the Nernst Planck equations10,13, which take into account the exchange of ions having different mobility to determine the various physical parameters, is, therefore, applied. The physical parameters such as self-diffusion coefficient, $D_0$, energy of activation, $E_a$, and entropy of activation, $\Delta S^\circ$, have been calculated.

Experimental Procedure

Reagents and chemicals

Zirconyl chloride (ZrOCl$_2$·8H$_2$O) and sodium tungstate (Na$_2$WO$_4$·2H$_2$O) were obtained from Lobachemie (India). Orthophosphoric acid (H$_3$PO$_4$) was obtained from CDH product (India) while styrene was GSC product. All other reagents and chemicals were of Analar grade.

Kinetic measurements

The rate of exchange were measured by limited bath technique13 on exchanger particles of mean radius $(r_0)$=125 μm (50-70 mesh size). Twenty mL fractions of the 0.02 M metal ion solution ($\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, $\text{Cu}^{2+}$, $\text{Mn}^{2+}$, $\text{Ni}^{2+}$ and $\text{Zn}^{2+}$) were shaken with 200 mg of the exchanger in H$^+$ form in several stoppered conical flasks at the desired temperatures [25, 33, 50 and 65(±0.5) °C] for different time intervals (0.5, 1.0, 2.0, 3.0 and 4.0 min). Supernatant liquid was immediately removed and determinations were done by EDTA titrations14.

Results and Discussion

Kinetic studies illustrate that the ion-exchange process of SZWP is controlled by particle diffusion at and above a metal ion concentration of 0.02 M. Below this concentration, film diffusion is more prominent. 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:

$$U(\tau) = \frac{\text{the total amount of exchange at time } \tau}{\text{the amount of exchange at infinite time}}$$
Plots of $U(\tau)$ versus $\tau$ (min) (Fig. 1) for all metal ions indicate that the fractional attainment of equilibrium is faster at a higher temperature suggesting that the mobility of the ions increases with an increase in temperature. Each value of $U(\tau)$ has a corresponding value of $\tau$ (dimensionless time parameter) obtained on solving Nernst-Planck equations:

$$U(\tau) = \{1 - \exp[-\pi^2(f_0(\alpha)\tau + f_0(\alpha)\tau^2 + f_0(\alpha)\tau^3)]\}^{1/2}$$

where

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

and the mobility ratio $\alpha = \frac{D_M}{D_H}$, $r_0 =$ particle radius and $D_M$ is the interdiffusion coefficient of the metal ion.

The plots of $\tau$ versus time ($t$) (Fig. 2) at the four different temperatures, are the straight lines passing through the origin, confirming the particle diffusion controlled phenomenon for M(II)-H(I) exchanges at a metal ion concentration of 0.02 M. The slopes ($S$ values) of various $\tau$ versus time ($t$) plots for all metal ions are given in Table 1, which are related with $D_H$ as:

$$S = \frac{D_H}{r_0^2}$$

The values of $-\log D_H$ obtained by using the above equation give straight lines when plotted against $1/T$ (Fig. 3), verifying the validity of the Arrhenius equation:

![Fig. 1—Plots of $U(\tau)$ vs $t$ (time) for different metal(II)-H(I) exchanges at different temperatures on styrene supported zirconium(IV) tungstophosphate cation exchanger (▲) 25°C, (△) 33°C, (●) 50°C (●) 65°C](image-url)
Fig. 2—Plots of $\tau$ vs $t$ for different metal(II)-H(I) exchanges at different temperatures on styrene supported zirconium(IV) tungstophosphate cation exchanger (▲) 25°C, (◇) 33°C, (○) 50°C, (●) 65°C

Fig. 3—Plots of $-\log D_H$ vs $1/T(K)$ for (a) Mg$^{2+}$-●; Ba$^{2+}$-●; Ca$^{2+}$-▲; Sr$^{2+}$-▲; and (b) Mn$^{2+}$-X; Ni$^{2+}$-Θ; Cu$^{2+}$-●; Zn$^{2+}$-x on styrene supported zirconium(IV) tungstophosphate
Table 2—Values of $D_0$, $E_a$ and $\Delta S^*$ for some metal ions on styrene supported zirconium (IV) tungstophosphate (SZWP)

<table>
<thead>
<tr>
<th>Metal ion exchange with H(1)</th>
<th>Ionic mobility $\times 10^9$ (m$^2$·s$^{-1}$·mol$^{-1}$)</th>
<th>Ionic radii (nm)</th>
<th>$D_0$ (m·s$^{-1}$)</th>
<th>$E_a$ (kJ·mol$^{-1}$)</th>
<th>$\Delta S^*$ (J·K$^{-1}$·mol$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>Mg(II)</td>
<td>55×10$^{-9}$</td>
<td>7.8×10$^{-2}$</td>
<td>4.47×10$^{-10}$</td>
<td>7.59</td>
<td>-75.39</td>
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<td>Ca(II)</td>
<td>62×10$^{-9}$</td>
<td>10.6×10$^{-2}$</td>
<td>4.62×10$^{-10}$</td>
<td>9.02</td>
<td>-73.48</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>62×10$^{-9}$</td>
<td>12.7×10$^{-2}$</td>
<td>7.04×10$^{-10}$</td>
<td>9.79</td>
<td>-71.61</td>
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<td>Ba(II)</td>
<td>66×10$^{-9}$</td>
<td>14.3×10$^{-2}$</td>
<td>1.06×10$^{-9}$</td>
<td>10.19</td>
<td>-68.21</td>
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<tr>
<td>Cu(II)</td>
<td>57×10$^{-9}$</td>
<td>7.0×10$^{-2}$</td>
<td>7.08×10$^{-10}$</td>
<td>9.54</td>
<td>-71.57</td>
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<tr>
<td>Ni(II)</td>
<td>52×10$^{-9}$</td>
<td>7.8×10$^{-2}$</td>
<td>3.80×10$^{-10}$</td>
<td>8.39</td>
<td>-76.74</td>
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<tr>
<td>Mn(II)</td>
<td>55×10$^{-9}$</td>
<td>9.1×10$^{-2}$</td>
<td>5.37×10$^{-10}$</td>
<td>8.65</td>
<td>-73.86</td>
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<tr>
<td>Zn(II)</td>
<td>56×10$^{-9}$</td>
<td>8.3×10$^{-2}$</td>
<td>1.26×10$^{-9}$</td>
<td>11.63</td>
<td>-66.78</td>
</tr>
</tbody>
</table>

$D_0 = D_0 \exp(-E_a / RT)$  

$D_0$ is obtained by extrapolating these lines and observing the intercepts at the origin. The activation energy, $E_a$, is then calculated from Eq. (4) putting the value of the $D_0$ corresponding to the $T$ value as 273 K in the graph. The entropy of activation, $\Delta S^*$, was then calculated by substituting $D_0$ in the equation:

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

where $d$ is the ionic jump distance taken as 5 Å, $k$ is the Boltzmann constant and $h$ is Planck’s constant, $T$.
is taken as 273 K. The values of diffusion coefficient, $D_0$, energy of activation, $E$, and entropy of activation, $\Delta S^\circ$, obtained are summarized in Table 2. Negative values of entropy of activation suggest a greater degree of order achieved during the metal(II)-H(I) exchange process.

This study also indicates that the value of $E$, and $\Delta S^\circ$ have linear relations with ionic radii, hydrated radii and ionic mobilities for alkaline earth metals (Fig. 4). But in case of the transition metal ions studied this behaviour is not observed. Rather, they show an irregular variation. It may be due to a more distinct variation in the ionic radii in alkaline earth metals than in transition metals selected for this study.

Acknowledgement

The authors are thankful to Professor K.G. Varshney, Chairman, Department of Applied Chemistry, Aligarh Muslim University, Aligarh, for providing research facilities to carry out this work.

References