PHYSICAL CHEMISTRY, VOL.13, PP 31-37, 1994

KINETICS OF PHOSPHATE/SULPHATE EXCHANGE STUDIES ON AMBERLITE IRA-400

S.MUSTAFA, SAMAD YAR HUSSAIN,
NASIM REHANA AND M.SAFDAR

National Centre of Excellence in Physical Chemistry,
Peshawar University, Peshawar, Pakistan

*Chemistry Department, Azad Jammu and Kashmir University,
Muzaffarabad, Pakistan

(Received on 8th December, 1994)

ABSTRACT

The kinetics of phosphate/sulphate exchange on the strong basic anion exchanger, Amberlite IRA-400 has been studied as a function of temperature and at two different concentrations. The film and particle diffusion coefficients and the activation parameters of the process are calculated.

INTRODUCTION

Though the kinetics of anion exchange sorption is of great importance in order to understand the mechanism of the process, yet very few attempts have been made to study the kinetics of oxyanions under different experimental conditions such as pH, temperature, nature of counterion and others [1,2]. The reason being the complexity of the process, as they involve different ionic species under different experimental conditions. The present paper deals with the factors governing the rate of exchange of phosphate/sulphate anions on strong basic anion exchanger, Amberlite IRA-400.
MATERIALS AND METHODS

Materials

The resin, Amberlite IRA-400 (30 mesh), a strong basic anion exchange resin was washed several times with distill water in a burette provided with a glass wool plug. The resin was conditioned by treating with three to four times with 100 mL portions of 1M H₂SO₄. The treatment continued until the concentration of the effluent also became equal to 1M. The whole system was left standing for 24 hours and washed until the washing water was free of SO₄²⁻. After air-drying, the resin was stored for kinetic studies.

Procedure

An exactly weighed amount (1 g) of the resin was mixed with 250 mL of KH₂PO₄ solution in 500 mL Erlenmeyer flask. Two different initial concentrations (0.807 mmol.L⁻¹ and 4.843 mmol.L⁻¹) of phosphate were used. The mixture placed in an air thermostat at the desired temperature. After different time intervals, small portions (1 mL) of the solution were taken out. The phosphate ion concentration in the aqueous phase was determined by the method of Murphy and Riley [3].

RESULTS AND DISCUSSION

The results of the study are presented in Figures 1 and 2 which show that rate of phosphate sorption depends upon the concentration of phosphate in solution and the temperature. The shape of the curves show that phosphate sorption initially being rapid, is followed by a slow process when the concentration of the solution is decreased. It is also evident from these figures that the equilibrium is attained in 180 minutes for low phosphate concentration while for high phosphate concentration the time needed is 260 minutes. The rate of phosphate sorption on the sulphate form of the resin is much slower than the phosphate/hydroxide and phosphate/chloride exchange studies, reported in our earlier work [2], where the equilibrium was attained in 30-60 minutes for the similar phosphate concentrations. This may be due
Fig. 1. Amount of phosphate adsorbed as a function of time for $SO_4^{2-}$ form of the resin at different temperatures (conc. = 0.807 mmol/L).

Fig. 2. Amount of phosphate adsorbed as a function of time for $SO_4^{2-}$ form of the resin at different temperatures (conc. = 4.843 mmol/L).
to the greater selectivity of the resin towards the divalent sulphate anion as compared to monovalent chloride and hydroxide anions.

The mechanism of phosphate sorption by Amberlite IRA-400 (SO\textsubscript{4}\textsuperscript{2-} form) can be described with the help of either film or particle diffusion equation [4,5]. When the data of phosphate sorption at low phosphate concentration (0.807 mmol.L\textsuperscript{-1}) is plotted according to film diffusion equation, a straight line (Figure 3) is obtained while at high phosphate concentration (4.843 mmol.L\textsuperscript{-1}), the particle diffusion equation is found to be applicable (Figure 4).

The values of the film and particle diffusion coefficients, D\textsuperscript{f} and D\textsuperscript{i} [4] respectively are given in tables 1 and 2. It can be seen from these tables that both the diffusion coefficients increase with the increase in temperature. This behaviour is more prominent in low phosphate concentrations. Comparing the values of the phosphate diffusion coefficients presented here with those reported earlier [2], it is observed that the values of both the diffusion coefficient are dependent upon the nature of the counterion. The values of the film diffusion coefficients follow the sequence: \textit{OH}^\textsuperscript{-} > \textit{Cl}^\textsuperscript{-} > \textit{SO}_4\textsuperscript{2-} while a reverse i.e., \textit{SO}_4\textsuperscript{2-} > \textit{OH}^\textsuperscript{-} > \textit{Cl}^\textsuperscript{-} is observed in the case of particle diffusion coefficients. Such a reversal of the diffusion coefficients points towards atleast a partial dehydrations of the phosphate ions before they enter the ion exchanger.

Collecting the kinetic data at different temperatures (25°C-50°C), the energy of activation (Ea) of both the diffusion processes can be calculated according to the Arrhenius equation (tables 1 and 2). The larger energy of activation for the sulphate form of the resin shows that sulphate anions are strongly bound to polystyrene cation. The net activation entropy, \(\Delta S^*\) of the exchange can be estimated, using the Eyring reaction rate theory [6]. The values of \(\Delta S^*\) obtained at all temperatures are positive, showing the disorder caused in the exchanger through which fairly large anions HPO\textsubscript{4}\textsuperscript{2-} or SO\textsubscript{4}\textsuperscript{2-} are bound to inter-diffusion. This positive contribution to the activation entropy observed with anion exchanger is attributed to the large hydration charge of the mobile anions and
Fig. 4. Particle diffusion plots for SO$_4$- form of the resin at different temperatures (conc. = 4.843 mmol/L).

Fig. 3. Film diffusion plots for SO$_4$- form of the resin at different temperatures (conc. = 0.807 mmol/L).
Table 1
Kinetic parameters for the film diffusion process
(concentration = 0.807 mmol.L⁻¹).

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>D¹ x 10¹⁰ (cm² sec⁻¹)</th>
<th>Ea (kJ mol⁻¹)</th>
<th>ΔG² (kJ mol⁻¹)</th>
<th>ΔH¹ (kJ mol⁻¹)</th>
<th>ΔS¹ (kJ mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.05</td>
<td>-48.4</td>
<td>3.0</td>
<td>0.173</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>9.23</td>
<td>-49.9</td>
<td>3.0</td>
<td>0.176</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>9.36</td>
<td>-50.7</td>
<td>2.9</td>
<td>0.174</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>9.60</td>
<td>-53.5</td>
<td>2.9</td>
<td>0.174</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>9.80</td>
<td>-53.2</td>
<td>2.8</td>
<td>0.173</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Kinetic parameters for the particle diffusion process
(concentration = 4.843 mmol.L⁻¹).

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>D¹ x 10⁸ (cm² sec⁻¹)</th>
<th>Ea (kJ mol⁻¹)</th>
<th>ΔG² (kJ mol⁻¹)</th>
<th>ΔH¹ (kJ mol⁻¹)</th>
<th>ΔS¹ (kJ mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.40</td>
<td>-68.6</td>
<td>16.5</td>
<td>0.290</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3.60</td>
<td>-70.4</td>
<td>15.4</td>
<td>0.290</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>3.60</td>
<td>-71.8</td>
<td>16.5</td>
<td>0.296</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>3.60</td>
<td>-73.1</td>
<td>16.4</td>
<td>0.285</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>5.40</td>
<td>-74.1</td>
<td>16.3</td>
<td>0.280</td>
<td></td>
</tr>
</tbody>
</table>

of the structure bound cationic exchange groups in the resin. Further, the large positive values of ΔS⁺ observed in the present study as compared to the negative values reported previously by us [2], also show a partial weakening of the ion exchanger-phosphate bond in comparison to ion exchanger-sulphate bond in the present case. Similar positive values of ΔS⁺ ranging between 7.5 and 41.8 J mol⁻¹ deg⁻¹, were obtained by Zaki [7] for resin cross-linkage ranging between 4 and 6% DVB.
The values of enthalpy and free energy of activation are calculated using the following equations:

\[
\Delta H^* = E_a - RT \tag{1}
\]
\[
\Delta G^* = \Delta H^* - T\Delta S^* \tag{2}
\]

The values of enthalpy of activation (\(\Delta H^*\)) and free energy of activation (\(\Delta G^*\)) are listed in tables 1 and 2. The values of \(T\Delta S^*\) being greater than \(\Delta H^*\) negative values of \(\Delta G^*\) are obtained. The positive values of \(\Delta H^*\) point towards the endothermic nature of the process while the positive values of \(\Delta G^*\) show the non-spontaneous nature of the phosphate/sulphate exchange on the resin, Amberlite IRA-400.

REFERENCES


5. D.Reichenberg, ibid, 75, 589 (1953).
