THE ADSORPTION OF PHOSPHAMIDON ON THE SURFACE OF ANTIMONY (V) PHOSPHATE: A THERMODYNAMIC STUDY
INTRODUCTION

The use of pesticides has been a regular practice in our society as they greatly improve the yields of farms, facilitate storage, and even control the spread of insect-borne diseases. However, an excessive and frequent application of pesticides has led to the increasing concerns about the residues that are left in the environment, as they are likely to be taken in by the humans through the food they eat, the water they drink, and the air they breath. Because of this, the toxicity of pesticides at residual concentrations has become a popular focus of interest for toxicologists, environmentalists, chemists and biochemists. The adsorption of pesticides on soils has been a significant feature (1-4), which is affected by the presence of metal ions in soils as they have an important role in modifying its nutritional status.

Inorganic ion exchangers are known to be selective for various metal ions (5) and hence their presence in soil may have some far-reaching consequences. A preliminary study has revealed that these materials are likely to increase the adsorption capacity of soils for pesticides when mixed with them (6-8). In order to explore further this behaviour of inorganic ion exchangers for different pesticides, a broad-spectrum systemic insecticide,
phosphamidon (C\textsubscript{10}H\textsubscript{19}ClNO\textsubscript{5}P) has been selected here as an adsorbing species and antimony (V) phosphate (SbP) as an adsorbent. The results of the thermodynamic study of the system are summarized in the following pages.
EXPERIMENTAL

Reagents and Chemicals:

Antimony (V) chloride (SbCl₅) (Fluka, Switzerland) used in this study was of approximately 98% purity and the trisodium orthophosphate (Na₃PO₄·12H₂O) was a BDH (Poole, England) product. Phosphamidon was obtained from Hindustan Ciba Geigy Ltd. (India). All other reagents and chemicals were of AnalyR grade.

Apparatus:

A waterbath incubator-shaker having a temperature variation of ±0.5°C was used for all the equilibrium studies. The spectrophotometric studies were made using a Bausch and Lomb Spectronic-20 spectrophotometer.

Preparation of the Reagent Solutions:

A stock solution (1.58M) of antimony (V) chloride was prepared in 4M HCl to avoid its hydrolysis. Further dilutions were also made in 4M HCl. Trisodium orthophosphate was dissolved directly in demineralized water (DMW) to prepare its solution of a desired concentration.

Synthesis of Antimony (V) Phosphate Cation Exchanger:

Antimony (V) phosphate was synthesized (9) as follows:
Antimony (V) chloride (0.1M) and trisodium orthophosphate (0.05M) solutions were mixed in a volume ratio 1:1 adjusting the pH of the solution at 0-1. The gel thus obtained was kept for 24 hours at room temperature (~30°C) and filtered by suction. The excess acid was removed by washing with DMW and the material was dried in an air oven at 45°C. It was then cracked into small granules by putting in DMW, and these were converted into the H⁺-form by treating with approximately 1M HNO₃ for 24 hours with occasional shaking and intermittently replacing the supernatant liquid. The material thus obtained was finally washed to a pH 6-7 and dried as above before sieving to a uniform size (60-100 mesh). The Na⁺- ion exchange capacity obtained by column process was found to be 1.75 meq/dry g.

**Adsorption Thermodynamics:**

Portions (0.2g) of the antimony (V) phosphate (H⁺-form) were taken in various stoppered conical flasks containing 20 ml phosphamidon solutions of different concentrations (100 to 1000 mg litre⁻¹) at the desired temperatures (30, 45 and 60°C) and the mixtures were shaken for 2 hours to attain equilibrium (Figure 3.1). The supernatant liquid, was then analyzed spectrophotometrically (10) for the presence of phosphamidon. The phosphamidon solutions were also analyzed similarly prior to their mixing with the exchanger to obtained the initial amount.
Fig. 3.1: Plots of adsorbed phosphamidon versus time on antimony (V) phosphate cation exchanger at three different temperatures.
RESULTS AND DISCUSSION

The adsorption of phosphamidon on antimony (V) phosphate at all the three temperatures (30, 45 and 60°C) is represented by the isotherms shown in Figure 3.2. All the isotherms adequately follow a Freundlich adsorption behaviour and can be represented by the equation

\[
x/m = K C^{1/n}
\]

where \(x/m\) is the surface concentration of phosphamidon in mmoles per gram of the exchanger, \(C\) is the equilibrium concentration of phosphamidon in mmoles ml\(^{-1}\) and \(K\) and \(1/n\) are the constants determined from the intercepts and slopes of the straight lines respectively (Figure 3.3) fitted to the points by the least squares method. The values so obtained are listed in Table 3.1.

Thermodynamic parameters are calculated from the variation of the thermodynamic equilibrium constant, \(K_o\), (or the thermodynamic distribution coefficient) with the change in temperature. \(K_o\) for the adsorption reaction can be defined as follows:

\[
K_o = \frac{a_s}{a_e} = \frac{\gamma_s}{\gamma_e} \cdot \frac{C_s}{C_e}
\]

where \(a_s\) is the activity of the adsorbed solute, \(a_e\) is the activity of the solute in solution at equilibrium, \(C_s\) is the
surface concentration of phosphamidon in mmoles per gram of exchanger, $C_e$ is the concentration of phosphamidon at equilibrium in mmoles ml$^{-1}$, $\gamma_s$ is the activity coefficient of the adsorbed solute, and $\gamma_e$ is the activity coefficient of the solute in solution.

As the concentration of the solute in the solution approaches zero, the activity coefficient approaches unity reducing equation 3.2 to the following form:

$$\lim_{C_s \to 0} \frac{C_s}{C_e} = \frac{a_s}{a_e} = K_0$$ .... 3.3

Values of $K_0$ are obtained by plotting $\ln (C_s/C_e)$ versus $C_s$ and extrapolating $C_s$ to zero (2). A straight line obtained, is fitted to the points based on least squares analyses. Its intercept with the vertical axis gives the value of $K_0$ (Figure 3.4). Standard free energy changes ($\Delta G^\circ$) for interactions are calculated (11) from the relationship:

$$\Delta G^\circ = -RT \ln K_0$$ .... 3.4

where $R$ is the universal gas constant and $T$ is the temperature in degrees Kelvin. The average standard enthalpy change ($\Delta H^\circ$) is then calculated from the well known Van't Hoff isochore equation:

$$\ln \left[ \frac{K_0T_3}{K_0T_1} \right] = -\frac{\Delta H^\circ}{R} \left[ \frac{1}{T_3} - \frac{1}{T_1} \right]$$ .... 3.5
and standard entropy changes ($\Delta S^\circ$) are calculated using the equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$  

The values obtained are shown in Table 3.2. A negative value of standard enthalpy change ($\Delta H^\circ$) indicates that the phosphamidon - exchanger interaction is an exothermic process. It is supported by the adsorption isotherms plotted at different temperatures (Figure 3.1). Since the free energy changes are negative accompanied by a positive entropy change, the reactions are spontaneous with a high affinity for phosphamidon (12). As the results indicate, the adsorption of phosphamidon on the surface of antimony (V) phosphate is about 55-60% of the total amount added. This value is higher as compared to the adsorption of carbofuran on antimony (V) silicate and tin (IV) arsenosilicate studied earlier (6,8).

The mechanism of adsorption of phosphamidon on the surface of the exchanger can be explained as follows:

The replaceable $H^+$ ions of the changer may get interacted with the carbonyl ($\text{C} = \text{O}$) and phosphonyl ($\text{P} = \text{O}$) groups present in the structure of phosphamidon thus causing a marked localization of the attractive forces as shown below:
The adsorption decreases with an increase in temperature probably because of the weaker forces of attraction operating at higher temperatures.
<table>
<thead>
<tr>
<th>Temperature</th>
<th>K</th>
<th>1/n</th>
</tr>
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<tbody>
<tr>
<td>30°C</td>
<td>2.53</td>
<td>1.10</td>
</tr>
<tr>
<td>45°C</td>
<td>2.42</td>
<td>1.09</td>
</tr>
<tr>
<td>60°C</td>
<td>2.31</td>
<td>1.07</td>
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</table>
### TABLE 3.2

VALUES OF VARIOUS THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF PHOSPHAMIDON ON ANTIMONY (V) PHOSPHATE CATION EXCHANGER AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>$K$</th>
<th>$\Delta G^\circ$ (k Cal/mol)</th>
<th>$\Delta S^\circ$ (k Cal/mol/deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperatures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30°C</td>
<td>137</td>
<td>-2.96</td>
<td>5.61x10$^{-3}$</td>
</tr>
<tr>
<td>45°C</td>
<td>125</td>
<td>-3.05</td>
<td>5.63x10$^{-3}$</td>
</tr>
<tr>
<td>60°C</td>
<td>113</td>
<td>-3.13</td>
<td>5.62x10$^{-2}$</td>
</tr>
</tbody>
</table>

$\Delta H^\circ$ (k Cal/mol) = -1.26
Fig. 3.2: Adsorption isotherms of phosphamidon on antimony (V) phosphate cation exchanger at three different temperatures.
Fig. 3.3: Freundlich isotherms for the adsorption of phosphamidon on antimony (V) phosphate cation exchanger at three different temperatures.
Fig. 3.4: Plots of $\ln \frac{C_{s}}{C_{e}}$ versus $C_{s}$ on antimony (V) phosphate cation exchanger at three different temperatures.
REFERENCES