Adsorption of nicotine on dickite

J. P. SINGHAL and G. K. GUPTA
Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh
STUDIES ON THE THERMODYNAMICS OF ZINC EXCHANGE IN MONTMORILLONITE

Jagdish P. Singhal and Girtaj K. Gupta

Chemical Laboratories, Faculty of Engineering and Technology, Muslim University, Aligarh, India

The ion exchange equilibria and mechanism of Zn exchange with Na montmorillonite has been studied with the help of adsorption isotherms and thermodynamic parameters. The exchange isotherms, K and $\Delta G^\circ$ values indicated a spontaneity of reaction and a higher preference of Zn for the montmorillonite surface. A stronger binding of Zn and changes in the hydration rates of Zn and Na with increase in order were suggested by enthalpy and entropy effects respectively. The surface phase activity coefficients and the excess thermodynamic functions were indicative of a nonideal heterogeneous exchange in which the mixture of ions on the montmorillonite surface was more stable and more tightly bound with significant differences in the hydration rates of the ions in the mixture with respect to the homo-ionic forms.

The adsorption of Zn and its reactions with clays and soils are receiving increasing attention. Zn deficiencies are common in plants growing on sodic soils. The process of ion exchange is important in plant nutrition. The cation exchange of Zn on montmorillonite as well as its exchange adsorption on soils have been studied by several workers (Elgably and Jenny, 1943; Jurinak and Bauer, 1956). In the study of ion exchange it has been noticed that although two ions may exchange stoichiometrically, they would not, in general, be preferred or bound equally strongly on a surface. In view of the importance of the nature of ion exchange, the exchange of Zn with Na-montmorillonite has been studied with the help of thermodynamic models of Gaines and Thomas (1953), El-Sayed et al. (1970), and Singhal and Singh (1973). It has been felt that such a study will be of considerable significance in understanding the mechanism of zinc interaction with Na-montmorillonite, a clay mineral which occurs widely in montmorillonitic sodic soils.

MATERIALS AND METHODS

The montmorillonite clay used in these studies was extracted from a Mississippi bentonite which was obtained from Ward's Natural Science Establishment, Rochester, New York. The suspension obtained by removal of organic matter and sedimentation was saturated several times with 1N NaCl and then centrifuged and washed to give less than two micron chloride-free Na-montmorillonite suspension. The concentration of the suspension was 14.6 g per litre.
For the determination of the cation exchange capacity of Na-montmorillonite (Na-CEC) a known volume of the suspension was treated with a mixture consisting of 1N CaCl₂ in 0.1N HCl and then estimating the amount of Na released (JACKSON, 1958). The value as calculated came out to be 90 meq. per 100 g clay.

For determination of time of exchange equilibrium at constant ionic strength three sets of 10 ml suspensions of Na-montmorillonite were treated with 1, 6, and 15 ml of 0.02N Zn(NO₃)₂ and 14, 9, and 0 ml of 0.03N NaNO₃ solutions respectively. The mixtures were shaken for 1 hr. Similar exchanges were carried out at 3, 6, and 9 hr also. At the end of the above specified time intervals the mixtures were centrifuged and Zn was estimated in the supernatant liquids by titration with a standard solution of EDTA. The amount of Zn exchanged at different time intervals was then obtained from the amount of Zn added minus Zn remaining in the supernatants. The results are illustrated by Fig. 1, curves 1–3. A time of 3 hr was found to be sufficient for attainment of equilibrium during the exchange.

Cation exchange in clays is also controlled by pH. For determination of pH suitable to carry out exchange studies, two sets of 10 ml suspensions of Na-montmorillonite were treated with 0.1N HNO₃ and 0.1N NaOH to obtain the desired levels of pH. Zinc exchange was then carried out at a constant ionic strength by shaking the mixtures with variable and required volumes of Zn(NO₃)₂ and Na-montmorillonite at a temperature of 30°C and a time of 3 hr. The results of the pH effect on exchange are recorded in Fig. 2, curves 1 and 2.

Since exchange of Zn with Na-montmorillonite was found to be unaffected by variation of pH from 4.5 to 6, the exchange isotherms were determined at pH = 5.0. This also avoided hydroxide precipitation. Ten ml samples of Na-montmorillonite were taken in a large number of glass-stoppered tubes and their pH adjusted to 5.0 by
adding 0.1N HNO₃. The suspensions were then treated with various but proportionate amounts of 0.02N Zn(NO₃)₂ and 0.05N NaNO₃ to provide a constant ionic strength and a constant volume (25 ml) for the exchange. The tubes were shaken at 30±0.1°C in the first set of experiments and 60±0.1°C in the second set for 3 hr in a thermostatic water bath. The mixtures were then immediately centrifuged, and Na and Zn estimated in the supernatants by flame photometry and titration with a standard solution of EDTA, respectively. The corresponding concentration of Na in the clay phase was obtained by subtraction of Na concentration in the supernatant from Na-CEC. Similarly the amount of Zn taken up by the clay surface in replacing Na was obtained by difference between the amount of Zn added and the amount of Zn left behind in the equilibrium suspension.

RESULTS AND DISCUSSION

The reaction between Zn ions in solution and Na ions on the montmorillonite surface can be represented by the equation:

\[ \overline{C}_{\text{Na}} + \overline{C}_{\text{Zn}} \Leftrightarrow \overline{C}_{\text{Na}} + \overline{C}_{\text{Zn}}. \]  

(1)

The concentrations of the ions concerned, in terms of equivalent ionic fractions, were calculated from the following expressions:

\[ X_{\text{Zn}} = \frac{\overline{C}_{\text{Zn}}}{\overline{C}_{\text{Na}}} - \frac{\overline{C}_{\text{Zn}}}{\overline{C}_{\text{Na}}} - \frac{\overline{C}_{\text{Na}}}{\overline{C}_{\text{Na}}} \times C_{\text{Na}}. \]

![Fig. 3. Exchange isotherms for zinc ion on Na-montmorillonite.](image)
where $\bar{C}$ was the total ion concentration in the clay phase and $C$ that in the solution. The values obtained for the equivalent ionic fractions at 30 and 60°C were plotted and the exchange isotherms obtained are given in Fig. 3.

Isotherms at both the temperatures were found to deviate from the diagonal indicating that at constant ionic strength Zn continuously replaced Na from the montmorillonite surface over the entire range of concentrations studied by us and that it had a higher preference for the clay surface than Na. The preference also varied with temperature, being higher at 30 than at 60°C.

For a further examination of the exchange behaviour in dilute montmorillonite suspensions the separation factors and selectivity coefficients (Helffferich, 1962) were calculated from the following respective expressions:

$$
\alpha_{Na} = \left( \frac{X_{Zn}}{X_{Na}} \right) \left( \frac{X_{Na}}{X_{Zn}} \right),
$$

Correcting the separation factor for interactions in the solution phase by introducing the factor

$$
K_c = \left( \frac{X_{Zn}}{X_{Na}} \right)^2 \left( \frac{X_{Na}}{X_{Zn}} \right)^2,
$$

where $x_{Na}$ and $x_{Zn}$ were the activity coefficients of the two ions in the solution phase. The values are given in Table 1. A plot of the effect of Zn concentration on selectivity.

<table>
<thead>
<tr>
<th>$X_{Zn}$</th>
<th>$X_{Na}$</th>
<th>$X_{Zn}$</th>
<th>$X_{Na}$</th>
<th>$K_c$</th>
<th>log $K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>0.996</td>
<td>0.157</td>
<td>0.843</td>
<td>5.6</td>
<td>0.75</td>
</tr>
<tr>
<td>0.014</td>
<td>0.986</td>
<td>0.150</td>
<td>0.850</td>
<td>4.7</td>
<td>0.66</td>
</tr>
<tr>
<td>0.023</td>
<td>0.977</td>
<td>0.141</td>
<td>0.854</td>
<td>3.9</td>
<td>0.60</td>
</tr>
<tr>
<td>0.026</td>
<td>0.974</td>
<td>0.135</td>
<td>0.852</td>
<td>3.5</td>
<td>0.59</td>
</tr>
<tr>
<td>0.048</td>
<td>0.952</td>
<td>0.127</td>
<td>0.847</td>
<td>3.0</td>
<td>0.56</td>
</tr>
<tr>
<td>0.091</td>
<td>0.909</td>
<td>0.120</td>
<td>0.842</td>
<td>2.5</td>
<td>0.54</td>
</tr>
<tr>
<td>0.164</td>
<td>0.836</td>
<td>0.113</td>
<td>0.837</td>
<td>2.0</td>
<td>0.52</td>
</tr>
<tr>
<td>0.250</td>
<td>0.750</td>
<td>0.105</td>
<td>0.833</td>
<td>1.5</td>
<td>0.50</td>
</tr>
<tr>
<td>0.350</td>
<td>0.633</td>
<td>0.097</td>
<td>0.828</td>
<td>1.0</td>
<td>0.48</td>
</tr>
<tr>
<td>0.438</td>
<td>0.530</td>
<td>0.089</td>
<td>0.824</td>
<td>0.7</td>
<td>0.46</td>
</tr>
<tr>
<td>0.488</td>
<td>0.470</td>
<td>0.081</td>
<td>0.819</td>
<td>0.4</td>
<td>0.44</td>
</tr>
</tbody>
</table>

For a further examination of the exchange behaviour in dilute montmorillonite suspensions the separation factors and selectivity coefficients (Helffferich, 1962) were calculated from the following respective expressions:

$$
\alpha_{Na} = \left( \frac{X_{Zn}}{X_{Na}} \right) \left( \frac{X_{Na}}{X_{Zn}} \right),
$$

Correcting the separation factor for interactions in the solution phase by introducing the factor

$$
K_c = \left( \frac{X_{Zn}}{X_{Na}} \right)^2 \left( \frac{X_{Na}}{X_{Zn}} \right)^2,
$$

where $x_{Na}$ and $x_{Zn}$ were the activity coefficients of the two ions in the solution phase. The values are given in Table 1. A plot of the effect of Zn concentration on selectivity.
coefficients is represented in Fig. 4. During the exchange, the selectivity quotient initially decreased, followed by a rise and then a fall at both the temperatures. Such a variation was indicative of significant interactions between Zn and Na-montmorillonite, the preference of Zn for the solid surface varying according to the nature of the curves (Fig. 4).

For a further examination of the equilibria, the thermodynamic equilibrium constant $K$ was calculated from the simplified relationship of Gaines and Thomas (1953):

$$\ln K = (Z_B - Z_A) + \int_0^1 \ln K_0 \, dR_{ZB},$$

where $Z_A$ was the valence of Na and $Z_B$ of Zn. For the derivation of the above simplified formula from Gaines' original relationship, it became necessary to assume that $\int_b^Z (b) = \int_a^Z (a)$, namely that the activity of water was constant. That this was so was borne out by the fact that the equilibria was carried out in dilute suspensions with a constant volume of water in the mixture.

The values of $K$ were obtained by evaluating the integral from the areas under the curves (Fig. 4) using the trapezoidal rule. The values are given in Table 2. A higher value of $K$ at 30°C than at 60°C indicated a higher preference of Zn for the clay at the lower temperature. Further, Zn was preferred over Na by montmorillonite.

The standard free energy of exchange, $\Delta G^0$ was calculated from the equation:

$$\Delta G^0 = -RT \ln K,$$

(5)
Table 2. Thermodynamic values of the Zn exchange on Na-montmorillonite at 30 and 60°C.

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>30°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>18.0</td>
<td>11.9</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (cal/mole)</td>
<td>-1742</td>
<td>-1628</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (cal/mole)</td>
<td>-2744</td>
<td></td>
</tr>
<tr>
<td>$\Delta S^\circ$ (cal/mole)</td>
<td>3.3</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

and the standard enthalpy change $\Delta H^0$ from van't Hoff isochore,

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

The standard entropy change, $\Delta S^0$ was then obtained by the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0.$$ 

The values are listed in Table 2.

During the exchange of Na with Zn over montmorillonite the free energy change was negative over both the temperatures, that at 30°C being still more negative than the one at 60°C. At both the temperatures the exchanges were, therefore, spontaneous, the order of preference being Zn > Na. The order of preference varied with temperature, being higher at 30 than at 60°C. The results were in accordance with the earlier inferences.

Negative enthalpy change (Table 2) indicated that the reaction was exothermic, or in other words the binding energy of 1 atom of Zn was lower than that of 2 atoms of Na. Thus Zn was more tightly bound to montmorillonite than Na. This was in accordance with the values of $K_c$ being higher than unity (Table 1). The exchange was also ruled by entropy effects. The entropy loss was indicative of a greater order produced in the forward reaction during Zn transfer to montmorillonite. Entropy change included two reactions which occurred in the interface and the solution. In going from solution to solid phase some of the water of hydration of Zn ions was removed to give a more orderly structure of Zn ions on the surface with resultant immobilization and reduction in the degrees of freedom of Zn ions on the clay surface. This contributed towards entropy loss. Further the passage of Na ions from solid to water resulted in their enhanced hydration with greater ordering of water and a further entropy loss. There is evidence to support these facts (GAST and KLOBE, 1971; BIGGAR and CHEUNG, 1973).

The surface phase activity coefficients of sodium and zinc ions were calculated from the following expressions (MARINSKY, 1966):

$$\ln f_{\text{sa}} = \frac{\Delta G^0}{RT} \ln K_c - \int_0^{\frac{\Delta H^0}{RT}} d\lambda_\text{sa},$$

The surface phase activity coefficients of sodium and zinc ions were calculated from the following expressions (MARINSKY, 1966):
Table 3. The surface phase activity coefficients, excess free energies, enthalpies and entropies of mixing $\Delta G^*_n$, $\Delta H^*_n$, $\Delta S^*_n$ for Na-Zn exchange on montmorillonite at 30 and 60°C.

<table>
<thead>
<tr>
<th>$x_{2n}$</th>
<th>$f_{2n}$</th>
<th>$f_{2n}$</th>
<th>$\Delta G^*_n$</th>
<th>$\Delta H^*_n$</th>
<th>$\Delta S^*_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.058</td>
<td>1.01</td>
<td>0.01</td>
<td>-53.7</td>
<td>-222</td>
<td>-0.56</td>
</tr>
<tr>
<td>0.075</td>
<td>0.95</td>
<td>0.04</td>
<td>-177.1</td>
<td>-330</td>
<td>-0.51</td>
</tr>
<tr>
<td>0.107</td>
<td>0.94</td>
<td>0.05</td>
<td>-230.8</td>
<td>-402</td>
<td>-0.57</td>
</tr>
<tr>
<td>0.166</td>
<td>0.99</td>
<td>0.04</td>
<td>-325.7</td>
<td>-511</td>
<td>-1.61</td>
</tr>
<tr>
<td>0.299</td>
<td>1.06</td>
<td>0.06</td>
<td>-497.1</td>
<td>-937</td>
<td>-1.45</td>
</tr>
<tr>
<td>0.395</td>
<td>1.12</td>
<td>0.09</td>
<td>-545.2</td>
<td>-710</td>
<td>-0.55</td>
</tr>
<tr>
<td>0.499</td>
<td>1.07</td>
<td>0.14</td>
<td>-364.9</td>
<td>-882</td>
<td>-1.05</td>
</tr>
<tr>
<td>0.562</td>
<td>0.98</td>
<td>0.20</td>
<td>-556.3</td>
<td>-1117</td>
<td>-1.85</td>
</tr>
<tr>
<td>0.650</td>
<td>0.62</td>
<td>0.31</td>
<td>-504.3</td>
<td>-803</td>
<td>-0.99</td>
</tr>
<tr>
<td>0.843</td>
<td>0.89</td>
<td>0.54</td>
<td>-321.1</td>
<td>-959</td>
<td>-2.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$x_{2n}$</th>
<th>$f_{2n}$</th>
<th>$f_{2n}$</th>
<th>$\Delta G^*_n$</th>
<th>$\Delta H^*_n$</th>
<th>$\Delta S^*_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.060</td>
<td>1.03</td>
<td>0.02</td>
<td>-136.3</td>
<td>-274</td>
<td>-0.41</td>
</tr>
<tr>
<td>0.074</td>
<td>0.97</td>
<td>0.06</td>
<td>-156.8</td>
<td>-396</td>
<td>-0.72</td>
</tr>
<tr>
<td>0.094</td>
<td>0.95</td>
<td>0.08</td>
<td>-188.1</td>
<td>-437</td>
<td>-0.75</td>
</tr>
<tr>
<td>0.141</td>
<td>0.98</td>
<td>0.07</td>
<td>-258.3</td>
<td>-500</td>
<td>-0.73</td>
</tr>
<tr>
<td>0.275</td>
<td>1.08</td>
<td>0.09</td>
<td>-405.0</td>
<td>-1052</td>
<td>-1.94</td>
</tr>
<tr>
<td>0.349</td>
<td>1.03</td>
<td>0.13</td>
<td>-458.9</td>
<td>-680</td>
<td>-0.66</td>
</tr>
<tr>
<td>0.462</td>
<td>1.01</td>
<td>0.20</td>
<td>-489.9</td>
<td>-906</td>
<td>-1.25</td>
</tr>
<tr>
<td>0.545</td>
<td>0.96</td>
<td>0.28</td>
<td>-475.8</td>
<td>-1304</td>
<td>-2.48</td>
</tr>
<tr>
<td>0.603</td>
<td>0.75</td>
<td>0.39</td>
<td>-448.3</td>
<td>-654</td>
<td>-1.22</td>
</tr>
<tr>
<td>0.824</td>
<td>0.74</td>
<td>0.68</td>
<td>-264.7</td>
<td>-1102</td>
<td>-2.52</td>
</tr>
</tbody>
</table>

The values are given in Table 3. The values were indicative of a nonideal system resulting in an increase in heterogeneity in the distribution of Na ions and a decrease in heterogeneity in case of Zn ions on the solid surface. The results found support from the work of DEIST and TALIBUDEEN (1967) on ion exchange in soils.

To further examine the deviation of the heterogeneous system from ideality, the excess thermodynamic functions for the system were calculated from the following expressions (VANSANT and UYTTERHOEVEN, 1972, Gast and KLOSE, 1971):  

$$\Delta G^*_n = RT \left( x_{2n} \ln f_{2n} + x_{Na} \ln f_{Na} \right),$$  

$$\Delta H^*_n = -RT \left( x_{2n} \frac{\partial \ln f_{2n}}{\partial T} + x_{Na} \frac{\partial \ln f_{Na}}{\partial T} \right),$$

and
The values are given in Table 3. The values of $\Delta G^\circ_m$ were negative at both the temperatures which meant that with respect to the pure forms the heterogeneous surface phases were more stable than they would be if the mixing were ideal, i.e., the deviation from ideality occurred in the sense of a more stable mixture. Negative enthalpies of mixing pointed to a more tightly bound mixture of Na and Zn ions. The negative entropies of mixing were a pointer to a nonideal state of the mixture and a significant heterogeneity at the surface. The difference in the hydration rates of the ions in the mixture resulted in a decrease in entropy with respect to the homo-ionic forms.

Acknowledgement. The authors are grateful to Prof. Mohan Qureshi for research facilities provided in the laboratories.

REFERENCES

Adsorption of nicotine on dickite

J P SINGHAL and G K GUPTA
Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh

A study of the adsorption of simple organic molecules plays an important part in understanding the mechanism of their interactions with soil clays. Adsorption of organic compounds on clay surfaces depends upon several factors such as strong cation dipole attractions, hydrogen bonding, solvation of cations by polar molecules, coordination, cation exchange reactions, van der Waals interactions, pH and other environmental conditions.

Clay minerals constitute the most important reactive surfaces of the soil. They have been reported to provide heterogeneous chemical spots in the form of sorbed water around cations, hydroxyls at the edges, lattice surface oxygens and electrical double layer of changing polarity at the edges. They possess electron accepting sites in form of exposed aluminium and transition metals in higher valency state at the edges. The location and distribution of exchange sites on clays is an important factor in the nature and extent of adsorption.

The mineral dickite, a polymorph of Al₄(Si₄O₁₀)(OH)₈, has a structure somewhat similar to kaolinite. It is believed to carry Lewis and Bronsted acidic sites on its edge crystal faces. Fordham has demonstrated the existence of positive and negative sites at the edges of dickites along with some basal surfaces. The behaviour of such clay minerals, both chemically and physically depends to a great extent upon their surface energetics.

Nicotine is a polar heterocyclic compound. It is an electron donor in which the aliphatic nitrogen of the pyrrolidine ring is the donor species. It is an important pesticide. Its importance in the functions of the central nervous system is well known. A study of the adsorption and interaction of pesticides is of great importance because processes such as effective pesticidal action, their mobility, persistence and toxicity in soils depend to a great extent upon the nature and interaction of the chemical with the silicate clays.

Adsorption isotherms and titration curves can be used to provide information on the mechanism of interaction of organics with
soils. Regular and discontinuous isotherms due to heterogeneities on the adsorbant surface have been observed. Giles et al. have classified the various shapes of adsorption isotherms with respect to the reaction mechanism concerned.

The primary objective of this work was to investigate the mechanism of adsorption and interaction of nicotine, a typical alkaloid on dickite, a void filling mineral of the algal limestones in its acid and base saturated forms in dilute clay water suspensions.

**Materials and Methods.** — The dickite used in these studies was a monomineralic A.P.I. sample No 15 from Mexico obtained from Wards Natural Science Establishment Inc., Rochester, New York. It was dispersed in a mortar by grinding it lightly with a pestle and distilled water. The less than 2 \( \mu \) fraction obtained by repeated dispersion and centrifugation was converted into Na-clay by saturating it with molar NaCl several times. It was then washed with distilled water till no chloride was detected with \( \text{AgNO}_3 \) and till the conductivity of the suspension became constant. Hydrogen saturated dickite was prepared just prior to the required experiments, as per Aldrich and Buchanan’s method, by ion exchange technique. The concentration of the suspensions varied from 2.0 to 9.0 g. of clay per litre of suspension.

The H-dickite samples were subjected to potentiometric and conductometric titrations with nicotine as well as with NaOH. The results are given vide Figs. 1-2.

Adsorption experiments were conducted with temperature around 30°C by taking 10 ml of the appropriate clay suspension in a number of glass stoppered tubes, and adding various amounts of nicotine solution (0.5 g per litre), and deionised water to obtain a fixed final volume. After intermittent shaking and standing for 72 hours the suspensions were centrifuged, their pH and electrical conductivity recorded and the residual nicotine estimated with standard HCl. The amount of absorbed nicotine was determined as the difference between the amounts of nicotine added and remaining. Adsorption isotherms were plotted between equilibrium concentration and moles of nicotine adsorbed per 100 g. clay (Fig. 3).

The adsorption data was examined with the help of X-ray diffraction. The X-ray analysis was done on acid and base saturated samples of < 2 \( \mu \) dickite, on samples treated with nicotine and glycerine. For X-ray analysis the samples were oriented on glass microslides from a water suspension at room temperature. They were then air dried, solvated with glycerol and heated at 550°C for 2 hours. Patterns were obtained using filtered Cu K radiation on a « Mikro-meta » goniometer at a speed of 2° per minute. Basal spacings in \( \AA \) deduced from the positions of 001 reflections are given in table II.

**Results and Discussion.** — The results of potentiometric and conductometric titrations of H-dickite with NaOH and nicotine are given vide table 1, figures 1-2. The figures (curves 3 and
4) also show the changes that occurred in the pH and conductance during adsorption of nicotine by acid and base saturated dickites. The figures in parentheses in the table indicate the pH at the inflection points. The meq. of base per 100 g. clay as obtained from the inflections gave the base exchange capacities.

Adsorption of nicotine on acid and base saturated dickites in dilute suspensions in the equilibrium concentration range of 0.0 to 1.0 mmole of nicotine per litre yielded isotherms vide Fig. 3. An examination of the isotherms revealed that the isotherm for hydrogen saturated dickite was similar to class 'H' isotherm as defined by Giles et al., and that for the sodium saturated system

![Graph 1](image1.png)

![Graph 2](image2.png)

---

**Table 1.** Main inflections and base exchange capacities of acid and base saturated dickites as obtained during titration and adsorption.

<table>
<thead>
<tr>
<th>Mineral form</th>
<th>Nicotine as titrant and absorbate</th>
<th>Sodium hydroxide as titrant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potentiometry</td>
<td>Conductometry</td>
</tr>
<tr>
<td>H-dickite</td>
<td>15.0 (5.2)</td>
<td>12.5</td>
</tr>
<tr>
<td>Na-dickite</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
TABLE 2 — Basal spacings of H, Na, nicotine, nucine and heated treated samples of dickite

<table>
<thead>
<tr>
<th>Nature of dickite</th>
<th>Basal spacings at 001 reflections in Å</th>
<th>Interlamellar separation in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-saturated dickite</td>
<td>7.07 (S)</td>
<td>—</td>
</tr>
<tr>
<td>Nicotine treated H-dickite</td>
<td>7.13 (W)</td>
<td>—</td>
</tr>
<tr>
<td>Na-saturated dickite</td>
<td>7.05 (S)</td>
<td>—</td>
</tr>
<tr>
<td>Nicotine treated Na-dickite</td>
<td>7.00 (M)</td>
<td>Nil</td>
</tr>
<tr>
<td>Nicotine complex treated with glycine</td>
<td>7.00 (W)</td>
<td>Nil</td>
</tr>
<tr>
<td>Na-saturated dickite at 550° C</td>
<td>Collapsed</td>
<td>—</td>
</tr>
<tr>
<td>Nicotine complex at 550° C</td>
<td>Collapsed</td>
<td>—</td>
</tr>
</tbody>
</table>

Letters in parenthesis in column II indicate intensities
S = strong, M = medium and W = weak.

similar to class ' L '. The adsorption in the two cases was thus very much different. The initial part in the case of the isotherm for the acid H-dickite was vertical indicating that nicotine had such a high affinity for the acid dickite that in dilute suspensions it was completely adsorbed till a limiting value (15.80 mmole/s) was reached at a point corresponding to complete saturation of its base exchange capacity and a pH = 7.10. An inflection or «knee» occurred at this point indicating completion of the first degree saturation. Such an initial steep rise was indicative of chemisorption with edge to edge ion attraction 
An increase in pH (Fig. 1, curve 3) and a decrease in electrical conductance (Fig. 2, curve 3) with an inflection similar to that obtained during titrations pointed to removal of protons during the interaction. The initial adsorption of nicotine on H-dickite, therefore, appeared to be due to the donation of electrons by nicotine to H-dickite resulting in coordination of its molecule as follows:

$$\text{CH}_2\text{N}^+\text{CH}_2\text{CH}_3 + \text{H-dickite} \rightarrow \left[ \begin{array}{c} \text{CH}_2\text{N}^+\text{CH}_2\text{CH}_3 \\ \downarrow \text{H} \end{array} \right]_{\text{dickite}}$$
The subsequent rise in adsorption beyond the inflection (Fig. 3, curve 1) pointed to an interaction of nicotine with the Bronsted or Lewis acid sites at the crystal edges of dickite. It has, however, been reported that Bronsted acid sites at the crystal edges of clays are not strong enough to react with weak bases like pyridine. Hence in the case of nicotine the Lewis acid character of dickite edges appeared to predominate. With aluminium at the edges thus acting as an electron acceptor and nicotine as an electron donor, a subsequent interaction resulted as follows:

\[
\text{N} + \text{Al} \rightarrow \text{N-}\text{Al} \quad \text{(dickite)}
\]

With the saturation of these sites the adsorption of nicotine in acid dickite became constant (Fig. 3, curve 1). This found support from the pH and conductance change which also became nearly constant (Figs. 1-2, curves 3) at this stage.

In spite of the greater deflocculation effect and larger surface area exposed by Na-dickite in comparison to H-dickite, a very small amount of nicotine was initially adsorbed by the sodium saturated dickite. This happened till an equilibrium concentration of 0.8 mmoles of nicotine was reached. As is often observed in cases of 'L' curves it thus appeared that nicotine molecules had some difficulty in finding vacant sites on the surface of Na-dickite. Fluctuations in the small adsorption were also observed in the earlier stages of the interaction suggesting changes from hydrophobic to hydrophilic nature in the clay system.

The nature of exchangeable cation in dickite thus seemed to determine the extent of adsorption. The order of adsorption found confirmation from the partial molar free energy changes that occurred during the interaction. The changes in partial molar free energy \( \Delta F \) were calculated from the thermodynamic relationship

\[
\Delta F = RT \ln \frac{C_e}{C_0}
\]

where \( C_e \) and \( C_0 \) were the equilibrium and initial concentration of the suspension respectively. An average of five values of \( \Delta F \) in case of H- and Na-saturated dickites yielded 301.0 and 204.3 cal/mol respectively, thus confirming the extent
of the driving force available for the adsorption of nicotine on the dickites.

The small amount of nicotine adsorbed in the earlier concentration range by Na-dickite and its marked difference from that observed in acid clay suggested that nicotine was adsorbed in this range through comparatively weak adsorptive forces at a binding site different from that in the case of the acid system. The interaction of nicotine with Na-dickite can be ascribed to formation of coordination bonds, capacity of nicotine to desorb water from around Na\(^+\) ions giving rise to proton transfers, hydrogen bonding with directly coordinated water and interaction with the weakly acidic sites at the edges. Possibility of coordination of nicotine to Na\(^+\) ions or proton transfers from adsorbed water would result in significant conductivity changes which were not observed in the present case. The small amount of adsorption of nicotine on Na-dickite in the early stages, therefore, appeared to be due to formation of hydrogen bonds between the pyrroolidine nitrogen of nicotine and the coordinated water as follows:

\[
\text{CH}_2-\text{CH}_2 + \text{dickite Na}--\text{OH}_2 \rightarrow \text{CH}_2-\text{CH}_2 \quad \text{dickite-} \text{O-H}^{+} \quad \text{N=CH}_3
\]

With the saturation of the above sites and crossing of the energy barrier, the electron acceptor Al or the weakly acidic hydroxyls at the edges of dickite took over and a sudden jump in chemisorption occurred vide equation (2), as in the case of acidic dickite (Fig. 3, curve 2), or vide equation (4) as follows:

\[
\text{N:} + \text{HO dickite} \rightarrow \text{N: H (Odickite)}^{-}
\]

There is evidence that clay surfaces even when saturated with basic cations act as weak to moderately weak acids\(^{18}\).
Examination of the nicotine-dickite complexes under X-ray diffraction did not yield any marked increase in basal spacing (Table 2). Treatment of the complex with glycerine showed no variation. Heat treatment at 550°C resulted in a complete collapse of the dickite peaks. These observations were in line with the fact that no lateral surface was available in dickite for the interaction with nicotine and only the edge sites took part in the interaction.

ACKNOWLEDGEMENT — Thanks are due to Prof. Mohsin Qureshi for providing laboratory facilities.

LITERATURE CITED

4) Fordham A W The location of iron-55, strontium-85 and iodine-125 sorbed by kaolinite and dickite particles Clays and Clay Minerals, 21, 175 (1973)
12) Parry E P An infrared study of pyridine adsorbed on acidic solids Characterization of surface acidity J Catalysis, 2, 371 (1963)
13) Ruskell J D Infrared study of the reactions of ammonia with montmorillonite and montmorillonite so-called Trans Faraday Soc, 61, 2284 (1965)
14) Schotfield R K and Samson H R Flocculation of kaolinite due to the attraction of oppositely charged crystal faces Diss Faraday Soc, 18, 133 (1954)
15) SinhaI J P and Singh C P Adsorption and reactions of nicotine on montmorillonites Indian J Chem, 10, 1100 (1972)
17) Solomon D H Clay minerals as electron acceptors or electron donors in organic reactions Clays and Clay Minerals, 16, 31 (1968)
19) Venuti L G and Gue A M. Discontinuity in adsorption processes with systems of solids and solutions Gazz Chem Ital 90, 254 (1960)
SUMMARY. — The adsorption of nicotine on acid and base saturated dickites yielded cation dependent adsorption isotherms similar to class « H » and « L » respectively. The pH, electrical conductivity changes and adsorption pointed to initial coordination of the nicotine molecule with H-dickite followed by interaction with the « Lewis » acid sites at the edges. Adsorption of nicotine on Na-dickite, on the other hand, was weak and mainly due to hydrogen bonding followed by chemisorption at the edges. X-ray diffraction provided evidence that only edge sites were involved in the reaction.

RÉSUMÉ. — Par l'adsorption de nicotine sur un acide ou une base saturée, on a obtenu d'isothermes d'adsorption, qui dépendent des cations et qui ressemblent à la classe « H » ou « L » respectivement. Les changements de pH, de conductivité et d'adsorption indiquent une coordination initiale entre les molécules de nicotine « Lewis » aux bords. L'adsorption de nicotine sur dickite de Na était, par revanche, faible et principalement à cause de bondage hydrogénique suivant la chemisorption aux bords. La diffraction des rayons X a mis en évidence le fait que seulement les bords s'impliquent à l'interaction.


RESUMEN. — La absorción de la nicotina en el ácido y la base de dickites saturada produjo isotermas de absorción dependiente de cationes semejantes a las clases « H » y « L » respectivamente. Los cambios de conductibilidad eléctrica pH y la absorción señalaron una coordinación inicial de las moléculas de la nicotina con la H-dickite seguida de una interacción con los sitios de ácido Lewis en los bordes. La absorción de la nicotina en la Na-dickite, por otro lado, era poca, debido, sobre todo, del vínculo del hidrógeno, seguido de chemisorption en los bordes. La difracción de los X-ray dio evidencia de que sólo los lugares de los bordes tomaron parte en la reacción.

RIASSUNTO. — L'assorbimento della nicotina su acido e base saturate dei dickites fornisce Catione dipendente da assorbimento di isotermi simili alla classe « H » e « L » rispettivamente. I cambiamenti di pH, di conducibilità e di assorbimento indicano una coordinazione iniziale della molecola della nicotina con H-dickite seguito dalla interazione con le posizioni dell'acido «Lewis» sui margini. L'assorbimento della nicotina su Na-dickite, d'altra parte, era debolmente a causa della lega dell'idrogeno seguito dall'assorbimento chimico ai margini. La diffrazione a raggi-X evidenzia che soltanto le posizioni ai margini erano implicate nella reazione.
Offprint from
THE JOURNAL OF SOIL SCIENCE
Volume 27 • Number 1 • March 1976

THERMODYNAMICS OF THE EXCHANGE OF NICOTINE ON ALUMINIUM-MONTMORILLONITE
J. P. SINGHAL, R. P. SINGH, C. P. SINGH, and G. K. GUPTA
(Faculty of Engineering and Technology, Muslim University, Aligarh, India)

OXFORD
AT THE CLARENDON PRESS
THERMODYNAMICS OF THE EXCHANGE OF NICOTINE ON ALUMINIUM-MONTMORILLONITE

J. P. SINGHAL, R. P. SINGH, C. P. SINGH, AND G. K. GUPTA
(Faculty of Engineering and Technology, Muslim University, Aligarh, India)

Summary
The ion exchange equilibria involving the interaction of nicotine with Al-montmorillonite was studied thermodynamically. The exchange isotherms at 30° and 60 °C indicated a preference for Al ions by montmorillonite as compared with nicotinium ions. A separation factor supported the conclusion. The enthalpy gain indicated tighter binding of Al. The entropy gain indicated a diffused and disordered arrangement of nicotinium ions in the Gouy layer with Al forming a more ordered arrangement in the Stern layer.

Introduction
A study of the adsorption of pesticide molecules plays an important part in understanding the mechanism of their interaction with soil clays. Nicotine is a cationic molecule in which the aliphatic nitrogen of the pyrrolidine ring is the electron-donor species. Clays constitute the most important reactive surfaces of the soil. They provide sites for cation exchange and many other reactions and form clay-organic complexes. In its aluminium-saturated form montmorillonite behaves as a Brønsted acid (Lloyd and Conley, 1970) to supply protons to nicotine in aqueous medium, as has been shown for many amines. With nicotine it can undergo the following exchange reactions

\[
\text{CH}_5\text{CH} \rightarrow \text{CH}, \text{N} \quad \text{CH} \rightarrow \text{CH}, \text{N} - \text{CH}_3 + \text{Al}^3+ \text{montmorillonite} + 3\text{H}_2\text{O} \rightleftharpoons \text{CH}_5\text{CH} \rightarrow \text{CH}, \text{N} \quad \text{CH} \rightarrow \text{CH}, \text{N} - \text{CH}_3 + \text{Al(OH)}_3^{3+} + \text{Mont}^3+\text{Al(OH)}_3
\]

Investigations in these laboratories revealed that the above reaction was reversible (Singhal and Singh, 1976).

The importance of a study of the retention of complex pesticides such as nicotine on acid soils led us to investigate the action of nicotine on Al-montmorillonite with the help of exchange isotherms and thermodynamic parameters. The treatment is mostly based on the thermodynamic treatment of previous workers (Gaines and Thomas, 1953; Howery and Thomas, 1965; Singhal and Singh, 1973).

Experimental
The clay was montmorillonite from Polkville, Mississippi, with a cation exchange capacity of 90 me/100 g clay as determined by the ammonium acetate method. It was dispersed, and the < 2 μm clay was separated by
EXCHANGE OF NICOTINE ON AI-MONTMORILLONITE

centrifugation and converted into Na-montmorillonite by treatment with 2M NaCl. Al-montmorillonite suspension was prepared from the Na-clay by saturating it repeatedly with 0.33M AlCl₃ at pH 3.2 and washing with deionized water to remove the excess salt. The pH of the resultant suspension was 5.1. Treatment of the Na-clay with AlCl₃ resulted in a reduction of the CEC. The CEC of the Al-montmorillonite, determined by extraction of the Al-saturated suspension with a solution of 0.1M HCl in 1M NaCl (Frink and Pech, 1963) was 70 me/100 g montmorillonite.

The concentration of Al-montmorillonite suspension was 8.5 g per litre. It showed an ageing effect for the first 24 h, shown by a slight increase of aluminium in the supernatant liquid. During the next 12 h the concentration of soluble aluminium was constant. The exchange experiments were conducted during this period to avoid any significant effects of ageing.

The exchange isotherms were determined by placing 10 ml samples of Al-montmorillonite in a number of glass-stoppered tubes. Various amounts of 0.03077M nicotine were added and the volume was made up to 25 ml with distilled water. The tubes were shaken for 12 h at 30±0.1 °C in the first set of experiments and 60±0.1 °C in the second set to attain equilibrium. The mixtures were centrifuged and aluminium and nicotine estimated in the supernatant liquids. Aluminium was estimated colorimetrically using aluminon (Jackson, 1958) as colour reagent, and nicotine with standard HCl using methyl red as indicator. The corresponding concentration of aluminium in the clay phase was obtained by difference (Al-CEC minus concentration of the cation in the supernatant liquid) and that for nicotine from nicotine added minus the nicotine in the supernatant liquid.

Results and discussion

The exchange reaction between nicotine and Al-montmorillonite in dilute suspensions can be described by the equation:

\[ C'_{\text{Al}} + C'_{\text{nicotine}} \rightleftharpoons C'_{\text{Al}} + C_{\text{nicotine}} \]

- The barred-quantities refer to the equivalent concentrations of each ion in the clay phase, and the unbarred to the concentrations in the solution. The equivalent ionic fractions (X) of nicotine and aluminium in montmorillonite and in solution were calculated from the expressions

\[ X'_{\text{nicotine}} = \frac{C_{\text{nicotine}}}{C'} \]

\[ X_{\text{nicotine}} = \frac{C_{\text{nicotine}}}{C} \]

\[ X'_{\text{Al}} = \frac{C'_{\text{Al}}}{C'} \] and \[ X_{\text{Al}} = \frac{C_{\text{Al}}}{C} \], where C and C were the total amounts of aluminium and nicotine in the clay and solution phases respectively.

The values obtained both at 30° and 60 °C are shown in Fig. 1. The deviation of the isotherms from the diagonal indicated a strong preference by montmorillonite for aluminium as compared with nicotine at both the temperatures over the entire range of concentration studied.
The affinity of montmorillonite for nicotine was further examined by the separation factor:

$$\alpha_{\text{nicotine}}^{\text{Al}} = \frac{X_{\text{nicotine}}}{X_{\text{Al}}} \cdot \frac{X_{\text{Al}}}{X_{\text{nicotine}}}.$$  \hspace{1cm} (2)

Values lower than unity (Table 1) at both temperatures indicated a higher preference by montmorillonite for trivalent Al than for the organic ion. However, the preference for nicotine as indicated by the separation factor increased with an increase in its concentration to a certain concentration of nicotine ($X_{\text{nicotine}}$) after which it declined. The separation factor was also larger at the higher temperature (Table 1) indicating an increase in the preference for nicotine with rise in temperature.

Taking the ratio of activity coefficients as unity (Robinson and Stokes, 1959) in the dilute range of concentration studied, the selectivity
EXCHANGE OF NICOTINE ON Al-MONTMORILLONITE

Table I

Values of equivalent ionic fractions of aluminium and nicotine and selectivity quotients at 30° and 60 °C for the nicotine exchange with Al-montmorillonite

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>$X_{Al}$</th>
<th>$X_{Al}$</th>
<th>$X_{nicotine}$</th>
<th>$X_{nicotine}$</th>
<th>$a_{nicotine}^{nicotine}$</th>
<th>$K_c$</th>
<th>Log $K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 °C</td>
<td>60 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.948</td>
<td>0.947</td>
<td>0.843</td>
<td>0.852</td>
<td>0.156</td>
<td>0.296</td>
<td>0.0234</td>
</tr>
<tr>
<td>2.</td>
<td>0.901</td>
<td>0.900</td>
<td>0.735</td>
<td>0.099</td>
<td>0.265</td>
<td>0.305</td>
<td>0.0438</td>
</tr>
<tr>
<td>3.</td>
<td>0.819</td>
<td>0.817</td>
<td>0.590</td>
<td>0.181</td>
<td>0.410</td>
<td>0.318</td>
<td>0.0616</td>
</tr>
<tr>
<td>4.</td>
<td>0.692</td>
<td>0.690</td>
<td>0.435</td>
<td>0.307</td>
<td>0.595</td>
<td>0.342</td>
<td>0.1007</td>
</tr>
<tr>
<td>5.</td>
<td>0.599</td>
<td>0.597</td>
<td>0.353</td>
<td>0.401</td>
<td>0.647</td>
<td>0.365</td>
<td>0.1403</td>
</tr>
<tr>
<td>6.</td>
<td>0.525</td>
<td>0.523</td>
<td>0.317</td>
<td>0.475</td>
<td>0.683</td>
<td>0.420</td>
<td>0.2031</td>
</tr>
<tr>
<td>7.</td>
<td>0.467</td>
<td>0.465</td>
<td>0.286</td>
<td>0.533</td>
<td>0.713</td>
<td>0.458</td>
<td>0.2557</td>
</tr>
<tr>
<td>8.</td>
<td>0.465</td>
<td>0.463</td>
<td>0.178</td>
<td>0.535</td>
<td>0.822</td>
<td>0.249</td>
<td>0.1055</td>
</tr>
<tr>
<td>9.</td>
<td>0.437</td>
<td>0.433</td>
<td>0.121</td>
<td>0.563</td>
<td>0.879</td>
<td>0.177</td>
<td>0.0727</td>
</tr>
<tr>
<td>10.</td>
<td>0.423</td>
<td>0.422</td>
<td>0.099</td>
<td>0.577</td>
<td>0.909</td>
<td>0.135</td>
<td>0.0544</td>
</tr>
<tr>
<td>11.</td>
<td>0.399</td>
<td>0.397</td>
<td>0.078</td>
<td>0.601</td>
<td>0.922</td>
<td>0.127</td>
<td>0.0541</td>
</tr>
<tr>
<td>12.</td>
<td>0.370</td>
<td>0.369</td>
<td>0.079</td>
<td>0.630</td>
<td>0.921</td>
<td>0.146</td>
<td>0.0683</td>
</tr>
<tr>
<td>13.</td>
<td>0.309</td>
<td>0.308</td>
<td>0.083</td>
<td>0.600</td>
<td>0.917</td>
<td>0.202</td>
<td>0.1144</td>
</tr>
</tbody>
</table>

$K_c = \frac{X_{nicotine}^{nicotine} X_{Al}}{X_{Al} X_{nicotine}^{nicotine}}$ (3)

A plot of the values of $K_c$ at 30° and 60 °C is given in Fig. 2.

For a further study of the affinity, the thermodynamic equilibrium constant $K$ was calculated from the relationship:

$\ln K_c = (Z_A - Z_B) + \int_{\theta}^{1} \ln K_c dX_{nicotine}$ (4)

where $Z_A$ and $Z_B$ were the charges on the competing ions. The integral was evaluated from the areas under the curves (Fig. 2) using the trapezoidal rule. The value of $K$ at 30 °C was lower than at 60 °C.
indicating that nicotine had a higher preference for montmorillonite at
the higher temperature (Vansant and Uytterhoeven, 1972).

The Gibbs free energy for the interaction was obtained by the
equation:

$$\Delta G^o = -RT \ln K.$$ (5)

The negative value of free energy implied a higher preference for
nicotine. That was, however, not conclusive because formation of

cicotininum clay was accompanied by an increase in enthalpy pointing
to a stronger binding of Al.

The standard enthalpy change was calculated from the Van't Hoff
isochore:

$$\ln \left( \frac{K_T}{K_{T_2}} \right) = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$ (6)

and the standard entropy change by the equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o.$$ (5)

The values given in Table 2 indicate that the interaction was affected
both by enthalpy and entropy effects. The positive value of enthalpy
suggested temperature-dependent adsorption and that nicotine was less
strongly bound on the montmorillonite surface than aluminium.

Entropy gain accompanying nicotine adsorption further justified this
assumption. It indicated a more diffuse and disordered arrangement

![Graph](image_url)

**Fig. 2.** Logarithms of selectivity quotients vs. equivalent ionic fraction of nicotine in montmorillonite.
Table 2

Thermodynamic values for the nicotine exchange with aluminium montmorillonite at 30° and 60°C

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>Values at 30 °C</th>
<th>Values at 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.51</td>
<td>1.90</td>
</tr>
<tr>
<td>ΔG° Cal/moles</td>
<td>-247</td>
<td>-424</td>
</tr>
<tr>
<td>ΔH° Cal/moles</td>
<td>1539</td>
<td>539</td>
</tr>
<tr>
<td>ΔS° Cal/moles</td>
<td>5.89</td>
<td>5.89</td>
</tr>
</tbody>
</table>

of nicotinium ions in the Goey layer with aluminium forming a more ordered arrangement in the Stern layer. Valence, electrostatic considerations, and the smaller size of Al ions as compared with the nicotinium ions justified the conclusion.

Acknowledgement

The second and third authors are indebted to C.S.I.R. (India) for the grant of senior and junior fellowships respectively.

REFERENCES


(Received 23 May 1974)
Effect of D-D Mixture on Availability of Some Plant Nutrients in a Black Cotton Soil

J. P. Singhal, Samiullah Khan and G. K. Gupta

Faculty of Engineering and Technology, Muslim University, Aligarh, U. P.

Abstract: The effects of D-D mixture, on major nutrient availability of a black cotton soil were examined. The results showed that while in smaller doses the fumigant significantly stimulated the availability of N and P, higher doses tended to be toxic. Lower doses had a non-significant suppressive influence on K availability. Organic matter was significantly reduced with increasing doses of D-D mixture. In general the stimulation after reaching a maximum gradually declined. The results have been explained on the basis of microbial activity. (Key words: D-D mixture; soil properties; black cotton soil).

Carbon disulphide, ethylene dibromide, methyl bromide, nemagon and telone have been extensively tried for the control of nematodes, fungi and other microbial pests (Minz & Palti 1954; Taylor 1951). The interaction of the fumigants with soil ingredients have been useful as well as inhibitory (Hanson & Nex 1953) to plant nutrients. The cumulative effects of adsorption, persistence and degradation of the nematocides in soil may result in toxic (Newhall 1951) and pollution hazards. The present work was undertaken with a view to examine the effects of a mixture (50:50) of 1,3 dichloropropene and 1,2 dichloropropane on organic matter and N, P, K of a black cotton soil.

EXPERIMENTAL

A black cotton soil sample (depth 0-30 cm) was collected from Kota district (Rajasthan, India). It was dried, crushed and sieved through 4 mm sieve. The general characteristics of the soil were: pH = 8.05, E.C. = 6.3 × 10⁻⁴ mhos/cm, available N = 0.0056%; available P = 0.0012%; available K = 0.0075%; org. matter = 0.68% and CaCO₃ = 3.5%.

The fumigant used was D-D, a mixture of 1,3 dichloropropene \( \text{Cl} - \text{H} - \text{C} - \text{C} = \text{C} \) and 1,2 dichloropropane \( \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \) of 1,3 dichloropropene \( \text{Cl} - \text{Cl} - \text{Cl} \) and 1,2 dichloropropane \( \text{H} - \text{H} \) with traces of other hydrocarbons. The chemical was obtained from M/s Burmah Shell (NOCIL), New Delhi.
The experiments were conducted in earthenware pots of 25 × 25 cm size which were coated with coal tar to prevent adsorption of water. Two kg of the soil was taken in each of the 18 pots. Zero day samples were drawn from the pots. The soil was then saturated to 25% by weight with distilled water. Six doses of D-D mixture (0.00, 0.25, 0.50, 0.75, 1.00 and 1.25 ml per kg soil) were injected at a depth of 15 cm in three replications without growing any crop. All the samples were watered with 150 ml distilled water per week throughout the period of experiment. Distilled water was used to avoid any contamination with impurities. Samples were periodically drawn from the pots at an interval of 15 days upto 90 days and the effects of the nematocide on N, P, K and organic matter examined.

Organic matter was estimated as per Walkley and Black (1947) method and available N as per alkaline KMnO₄ method (Subbiah & Asija 1956). Available P was determined colorimetrically by Olsen's (1954) method. Available K was estimated turbidimetrically (Datta et al. 1968) with Spectronic '20' at 660 μm.

RESULTS AND DISCUSSION

The effects of D-D mixture on organic matter, available N, P and K in black cotton soil are recorded in table 1. Each datum in the table for individual doses represents a mean of seven values recorded 0, 15, 30, 45, 60, 75 and 90 days after application of the fumigant. Similarly the average values for different days represent a mean of several values obtained at different doses, viz., @ 0.0, 0.25, 0.50, 0.75, 1.00, and 1.25 ml per kg soil. The data were subjected to statistical analysis of variance according to the two way classification and LSD values were calculated using the value of t at 5% level of significance. In the discussion that follows only the average values for doses and days have been considered and the term significant is used as meaning statistically significant at 5% F level (2.52 for doses and 2.42 for days).

Effect on Organic Matter

A reference to the data incorporated in table 1 show that as compared to the control, the amount of organic matter significantly decreased with increasing applications of the fumigant. With passage of time, however, it significantly increased, though still below the control, reached a maximum at 45 days and then significantly declined. The evidence for the decline in organic matter is provided by the fact that while fumigants like D-D greatly eliminate nematode population, many soil bacteria are fairly resistant to fumigants. The eradicant-type chemicals produce greater re-invasion potentials (Klemmer 1957) with the results that the reactivated soil organisms bring about a rapid decomposition of organic matter which significantly declines. Such effects have also been reported by Smith et al. (1947).

Effect on Available Nitrogen

Availability of N (Table 1) was found to significantly increase up to an application of 0.50 ml of the fumigant per kg of soil and upto 30 days. Thereafter a significant decline was observed in both cases.

The initial increase in available N was due to the decomposition of soil organic matter by fumigant resistant bacteria (Klemmer 1957) which resulted in the release of N. The decrease with large doses on the other hand appeared to be due to the inhibitory effects of large doses of the fumigant on nitrification (Koike 1961). The decline with passage of time was due to the dissipation of the toxic chemical and reinfestation of the high potential zones of the treated soil by the fast growing fungi of the vigorously competitive sugar and amino acid utilising kinds (Kreutzer 1965).

Effect on Available Phosphorus

A reference to table 1 revealed that the availability of P increased with application
TABLE 1

Effect of D-D mixture on nutrient availability for different doses of the mixture at various intervals of time.

<table>
<thead>
<tr>
<th>Treatment Doses (in ml per kg of soil) and duration (days)</th>
<th>Average values of available nutrients for various doses and days in mg per 100 g soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Org. matter</td>
</tr>
<tr>
<td>0.00</td>
<td>730.4</td>
</tr>
<tr>
<td>0.25</td>
<td>729.6</td>
</tr>
<tr>
<td>0.50</td>
<td>714.5</td>
</tr>
<tr>
<td>0.75</td>
<td>709.8</td>
</tr>
<tr>
<td>1.00</td>
<td>703.0</td>
</tr>
<tr>
<td>1.25</td>
<td>10.4</td>
</tr>
<tr>
<td>LSD</td>
<td>12.6</td>
</tr>
<tr>
<td>0 day</td>
<td>684.3</td>
</tr>
<tr>
<td>15 days</td>
<td>698.0</td>
</tr>
<tr>
<td>30 days</td>
<td>755.5</td>
</tr>
<tr>
<td>45 days</td>
<td>761.2</td>
</tr>
<tr>
<td>60 days</td>
<td>722.2</td>
</tr>
<tr>
<td>75 days</td>
<td>707.9</td>
</tr>
<tr>
<td>90 days</td>
<td>695.5</td>
</tr>
<tr>
<td>LSD</td>
<td>9.5</td>
</tr>
<tr>
<td>Variance ratio</td>
<td>82.4</td>
</tr>
</tbody>
</table>

of D-D mixture up to 0.75 ml/kg of soil and it reached a maximum value at 30 days. Higher doses and days reduced the availability. All the effects were statistically significant.

Several workers (Wensley 1953; Martin et al. 1957) have reported increased and highly stimulated microbial activity in soil as a result of fumigation. The action of ascomycetes, actinomycetes and the reinfestated fungal flora resulted in the decomposition of soil organic matter bringing about a gradual increase in P availability till a peak was reached both with doses and time. However, the toxic effect of too high doses and certain chemical reactions like reduction of P to PH₃ with passage of time resulted in the decline of P. Further work is, however, needed to establish the latter point.

**Effect on Available Potassium**

The effect of D-D on K availability with increasing doses was non-significant (Table 1). The up and down trend with passage of time though statistically significant followed the trend in the control. At the most, therefore, it could be said that D-D had a slight suppressive influence on K availability in soil. The mechanism by which this occurred was not entirely clear. Probably
the fumigant had a tendency to fix available K into non-exchangeable form on the clay lattice but further work is required to justify this conclusion.

ACKNOWLEDGEMENT

The authors are grateful to Dr. Abrar Mustafa Khan, Professor of Botany, Aligarh Muslim University, for helpful suggestions.

REFERENCES


Newhall, A. G. (1951) N. Y. State Flower Growers Bull. 73.

(Received: September, 1973; Accepted: June, 1974)
Effect of D-D Mixture on some Nutrients of a Saline Sodic Soil

J. P. SINGHAL, SAMIULLAH KHAN and G. K. GUPTA

Chemical Laboratories, Faculty of Engineering and Technology, Muslim University, Aligarh.

Manuscript received 5 April 1974; revised 18 September 1974; accepted 18 November 1974

The effects of different doses of D-D mixture, a well known nematocide, on some characteristics of a sodic saline soil were examined. The results revealed significant favourable and toxic responses of the fumigant on N, P, K and organic matter of the soil with passage of time. There was no marked effect on the pH and electrical conductivity. The results have been explained on the basis of microbial activity.

PESTICIDES are widely used in agricultural production. They are used as insecticides, herbicides, fungicides and nematocides. Their use is attendant with varied physical, chemical and biological changes in soils. Some work on the major nutrient availability in soils in presence of pesticides has been reported by Freney, Castro, Wedding et al., Alexander, Thiegs, as well as Shanker and Kumar. Their findings are, however, not entirely in agreement. Since the pH changes and nutrient availability have a profound influence on crop production, and since the use of pesticides in agriculture is increasing, it was thought worthwhile to examine the effects of different concentrations at various intervals of time of an important nematocide viz., a 50:50 mixture of 1,3 dichloro-propene and 1,2 dichloro-propane on the nutrient availability (N, P, K and organic matter) in a widely occurring sodic saline soil. Effects on pH and EC are also recorded.

Experimental

The soil used in the study (depth 0-30 cm) was collected from a representative area of Aligarh district. It was dried, crushed and sieved through 4 mm sieve. The general characteristics of the soil were determined and yielded the following data: pH = 9.31, E.C. = 26.3 \times 10^{-4} \text{ mhos cm}, available nitrogen = 0.0028\%, available phosphorous = 0.0006\%, available potassium = 0.0053\% and organic matter = 0.291\%.

The fumigant used was D-D, a mixture of 1,3 dichloro-propene \text{H--C--C=H} and 1,2 dichloro-propene \text{H--C--C--H} (50:50) with small amounts of other hydrocarbons.

The experiments were conducted in earthenware pots of 25 \times 25 cm size. The pots were cleaned and coated with coaltar to prevent adsorption of water. Two kg of the soil was taken in each of the 18 pots.

Zero day samples were then drawn from the pots. The soil was then saturated with 20\% distilled water by weight. Six concentrations of D-D mixture (0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 ml) were injected at a depth of 15 cm in three replications without growing any crop. All the samples were then watered with 100 ml distilled water per week throughout the period of experiments. Distilled water was used to avoid any contamination with impurities. Samples were drawn at an interval of 15 days up to 90 days and the effects of the nematocide on pH, EC, N, P, K and organic matter measured.

The pH of the samples was measured in 1:2 soil water suspension with a pH meter with glass and calomel saturated electrode assembly. Electrical conductivity was measured with Philips conductivity meter with dip type cell at 30° ± 1° on the 1:2 soil water suspension. Organic matter was estimated as per Walkley and Black's method. Available nitrogen was estimated as per alkaline KMnO₄ method. Available phosphorous was determined colorimetrically by Olsen's method. Available potassium was estimated turbidimetritically with turbidity measured by Bausch and Lomb spectronic '20' at 660 nm with a red filter.

Results and Discussion

The influence of D-D mixture on organic matter, available N, P, K of a sodic saline soil is expressed in Table 1. Each reading in the table for individual doses represents a mean of seven values recorded at 0, 15, 30, 45, 60, 75 and 90 days after application of the fumigant. Similarly the average values for different days represent a mean of several values obtained at different doses viz., 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 ml per 2 kg soil. The results were subjected to statistical analysis and variance ratio, and LSD values were calculated using the value of t at 5\% level of significance. In the discussion that follows, the average values for doses and days have been considered and the term significant is used as meaning statistically significant at 5\% F level (2.52 for doses and 2.42 for days).

Effect on pH and EC: No significant changes in pH or electrical conductivity either with increase in doses of D-D mixture or with interval of time was observed in the fumigated samples.
**Effect on organic matter:** The data given in Table 1 showed a significant decline in organic matter content of the soil with increasing applications of D-D mixture. With passage of time, however, there was a significant rise up to 30 days and thereafter a continuous decline. The decline in organic matter can be explained by the fact that while fumigates like D-D greatly eliminate nematode population, many soil bacteria are fairly resistant to fumigants. The eradicant type chemicals produce greater re-invasion potentials with the result that while fumigates like D-D greatly eliminate resistant to fumigants. The eradicant type chemicals with chlorinated insecticides.

**Effect on available nitrogen:** Examination of the data given in Table 1 generally indicated a significant increase in available nitrogen with increasing doses of D-D mixture up to a value of 1.5 ml per 2 kg of soil and thereafter followed a fluctuating pattern. The mechanism by which the fluctuation occurred was not entirely clear. The suppressive influence on potassium availability in soil was probably the tendency of the fumigant to fix available potassium into non-exchangeable form on the clay lattice but further work is required to justify this conclusion.

### Table 1—Effect of D-D Mixture on Nutrient Availability for Different Doses of the Mixture at Various Intervals of Time

<table>
<thead>
<tr>
<th>Applications :</th>
<th>Average values of available nutrients for various doses and days in mg per 100 gm soil</th>
<th>Organic</th>
<th>Nitrogen</th>
<th>Phosphor</th>
<th>Potassium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doses (in ml per two kg of soil)</td>
<td>Days</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>0 days</td>
<td>294.120</td>
<td>2.080</td>
<td>0.600</td>
<td>5.250</td>
<td></td>
</tr>
<tr>
<td>15 days</td>
<td>335.000</td>
<td>6.710</td>
<td>0.950</td>
<td>10.720</td>
<td>0.000</td>
</tr>
<tr>
<td>30 days</td>
<td>358.500</td>
<td>9.420</td>
<td>1.120</td>
<td>13.410</td>
<td>0.000</td>
</tr>
<tr>
<td>45 days</td>
<td>354.970</td>
<td>8.350</td>
<td>1.030</td>
<td>13.170</td>
<td>0.000</td>
</tr>
<tr>
<td>60 days</td>
<td>328.080</td>
<td>7.890</td>
<td>0.790</td>
<td>10.810</td>
<td>0.000</td>
</tr>
<tr>
<td>75 days</td>
<td>316.650</td>
<td>7.550</td>
<td>0.740</td>
<td>11.010</td>
<td>0.000</td>
</tr>
<tr>
<td>90 days</td>
<td>311.699</td>
<td>7.180</td>
<td>0.680</td>
<td>10.020</td>
<td>0.000</td>
</tr>
<tr>
<td>LSD</td>
<td>8.830</td>
<td>0.340</td>
<td>0.086</td>
<td>0.530</td>
<td></td>
</tr>
<tr>
<td>Variance ratio</td>
<td>65.050</td>
<td>334.450</td>
<td>42.750</td>
<td>215.420</td>
<td></td>
</tr>
</tbody>
</table>

**Effect on available phosphorus:** A reference to the results given in Table 1 generally indicated a significant increase in phosphorus availability up to 1.5 ml of D-D mixture per two kg of soil and up to 30 days of its application followed by a significant decline in both cases. Wensley and Martin and co-workers have reported increased and highly stimulated microbial activity in soil as a result of fumigation. The effects of reinfested fungus flora, ascomycetes and actinomycetes resulted in the decomposition of soil organic matter bringing about a gradual increase in phosphorous availability till a maxima was reached both with doses and passage of time. However, the toxic effect of too high doses, and certain chemical reactions like reduction of phosphorous to PHg with passage of time resulted in the decline of phosphorous.

### References

Acknowledgement
The authors are grateful to Dr. Abrar Mustafa Khan, Professor of Botany, Aligarh Muslim University, for helpful suggestions.
Spectrophotometric Studies on the Composition of Ammonia-Cobalt(II)-Dioxane Complex and its Application in the Estimation of Nitrogenas Kjeldahlised Ammonia

J. P. SINGHAL, SAMIULLAH KHAN AND G. K. GUPTA

Chemical Laboratory, Faculty of Engineering, Muslim University, Aligarh (U.P.)

(Manuscript received 10 May 1972; revised 11 August 1972; accepted 27 September 1972)

Ammonia when allowed to interact with cobalt(II) in presence of dioxane produced a yellowish brown colour in the pH range 5.5-7.5. The colour proved to be sufficiently specific to warrant a close spectrophotometric examination as regards to proper wavelength, reaction ratio, the effect of time and other variables such as concentration of dioxane. The $\lambda_{max}$ of the complex was found to be 390 nm and the reaction ratio by Job's method of continuous variation as 3:2. Results pointed to the possible application of this reaction for the spectrophotometric determination of Kjeldahlised nitrogen in soils and inorganic compounds.

A FEW methods for the determination of nitrogen are known. The most common of these methods is Kjeldahl's procedure where nitrogen is estimated as ammonia. Nessler's Reagent is sometimes used for the spectrophotometric determination of ammonia. Phenol hypochlorite reagent is also used. A sensitive, selective and easy method for the determination of Kjeldahlised nitrogen will be of immense importance in the estimation of combined nitrogen in various important materials like soils, fertilizers, explosives and high polymers.

It was noticed in these laboratories that when an aqueous solution of ammonia was treated with an aqueous solution of cobaltous chloride, a green precipitate was produced. This precipitate when dissolved in dioxane yielded a yellowish brown colour. The colour reaction appeared to be sufficiently specific. Therefore it was considered worthwhile to subject it to a close spectrophotometric examination as regards to the nature of the complex formed and the possibility of its application in the spectrophotometric determination of nitrogen as Kjeldahlised ammonia in ammonium salts and soils.

Experimental

Apparatus: The absorbance measurements were made on Bausch and Lomb Spectronic '20' spectrophotometer. Pyrex glassware was used for the preparation of solutions and for carrying out the experiments. pH was measured with Beckman pH meter model G.

Reagents: Standard solutions of cobaltous chloride, ammonia and dioxane were freshly prepared by dissolving requisite weights of pure grade Merek's reagents in double distilled water.

Procedure and Results:

Spectral curves: Absorption spectra were recorded at 30°C and in the pH range 5.5 to 7.5. The method of Vosburgh and Cooper was employed to ascertain the proper wavelength for carrying out spectrophotometric studies and to determine the number and nature of the complexes present in the colour. 0.005M solutions of cobalt and ammonia were mixed in the ratio 1:1, 1:2, 2:1, 4:1, 3:1 to 6 ml and to each of these 1.5 ml of 0.025M dioxane was added and the volume made up to 50 ml. Cobaltous chloride solution was used as a blank. The spectra showed a maxima at 390 nm (see Fig. 1, curves 1 to 4) in all cases, indicating that it was the most suitable wavelength for further spectrophotometric work. The results also pointed to the formation of only one complex in the above reaction.

Standard curve: A standard curve was drawn by distilling 0.02 g of NH₄Cl with 100 cc of 50% NaOH using Kjeldahl assembly and collecting the distillate in 25 ml of 0.1M Co(II) solution. Colour was then developed by adding 1.5 ml of 0.025M dioxane to various concentrations of the complex solution.

Fig. 1
absorbance taken and a standard curve drawn. Beer Lambert Law was followed from 0 to 280 ppm of nitrogen by the above distillate mixture in the pH range of 5.5 to 7.5.

Effect of dioxane concentration: Concentration of dioxane was found to affect the colour intensity. Best results were obtained on adding 180 ppm of dioxane to the complex solution.

Full colour development occurred in about 30 min. The colour was stable for nearly 3 hrs. Thenceafter precipitation occurred especially in the range of higher concentration.

Determination of reaction ratio: Job's method of continuous variation was used to determine the composition of complex formed in the solution. For this purpose equimolar concentration of ammonia and cobaltous chloride were mixed and the requisite amount of dioxane added. The sum of the concentration of ammonia and cobalt(II) was kept constant viz., $2.5 \times 10^{-4} M$, $2.0 \times 10^{-4} M$ and $1.66 \times 10^{-4} M$ respectively, while their ratio varied (see Fig. 2, curves a, b and c). A plot of absorbance against mole ratio of ammonia for measurement at 390 nm gave maxima at a mole ratio of 0.6 in all cases pointing to the presence of a 3 : 2 complex of ammonia and cobalt, i.e.,

$$3\text{NH}_3 + 2\text{Co}^{2+} \rightarrow \text{Co}_2(\text{NH}_3)_3^{4+}$$

Determination of nitrogen as Kjeldahlised ammonia in ammonium salts: 0.02 g of each of NH$_4$Cl and (NH$_4$)$_2$SO$_4$ were distilled with 100 ml of 50% NaOH in Kjeldahl flasks and nitrogen estimated as ammonia with the help of the standard curve using cobaltous chloride and dioxane as colour reagents.

Nitrogen in soils: 1 g of soil, 10 g K$_2$SO$_4$, 0.5 g CuSO$_4$. $3H_2O$, a few pieces of porcelain and 25 ml of conc. H$_2$SO$_4$ were taken in a Kjeldahl flask and shaken till the contents were well mixed. The mixture was digested till it became colourless (usually for 90 - 120 min). The flask was then cooled and 100 ml of water added. The mixture was distilled with 100 ml of 50% NaOH and a few fragments of granulated zinc. The distillate was collected in 25 ml of 0.1M CoCl$_2$·6H$_2$O solution and the volume made to 500 ml. Of this solution was taken in a 50 ml flask and colour developed with 1.5 ml of 0.025 M dioxane. After 30 min measurements were made on Bausch and Lomb spectronic "20" and the amount of nitrogen in soils calculated. Nitrogen was also determined as per usual Kjeldahl procedure. The results for amount of nitrogen obtained by the recommended method are given in Table 1.

<table>
<thead>
<tr>
<th>Material used</th>
<th>Cobalt(II) method</th>
<th>Acid method</th>
<th>Theoretical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$Cl</td>
<td>24.76</td>
<td>24.62</td>
<td>24.34</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>21.35</td>
<td>21.11</td>
<td>21.20</td>
</tr>
</tbody>
</table>

Table 1. Percentage of nitrogen as estimated by different methods

Discussion
An examination of the data obtained during the above investigations pointed to the definite possibility of the application of the colour reaction between ammonia, cobaltous chloride and dioxane for the detection and spectrophotometric estimation of Kjeldahlised ammonia in soils and in inorganic compounds. It is clear from table 1 that the results obtained by this method are almost of the same accuracy as the previous methods and can be successfully used for the determination of nitrogen in the case of soils and inorganic compounds. In the case of organic compounds, this method, however, failed to give satisfactory results.

Acknowledgement
Thanks are due to Dr. N. C. Saha and Dr. Mohsin Qureshi for providing research facilities.

References
RESUME

The study of soils can provide interesting information in the fields of science, agriculture and engineering. The surface phenomenon, the physico-chemical and pesticidal aspects are of vital importance in modern crop production and environmental pollution. The subject offers many fascinating opportunities for a chemist to investigate. Techniques such as those of adsorption, ion exchange, chemical thermodynamics, chemical kinetics and plant nutrition can lead to interesting results in the study of clay and soil interactions.

Systematic studies in the above direction started in the later part of the current century when workers like Hendricks\(^1\); Mortland\(^2\); Sweboda and Kunze\(^3\); Weber et al.\(^4\); Bailey et al.\(^5\); Giles et al.\(^6\); Gaines and Thomas\(^7\); Deist and Talibudeen\(^8\); Jurinak and Bauer\(^9\); Singhal et al.\(^10,14\); Boyd et al.\(^15\); Dunal et al.\(^16\); Seliferich\(^17\); Vansant and Dytterhoeven\(^18\) and Lindstrom et al.\(^19\) established a definite link between clay chemistry and physical chemistry.

During the last decade, interest in the use of pesticides in crop disease and control vastly increased in India. One of the serious deficiencies in the successful and wide-spread use of pesticides was a non-developed application of proper doses in the different types of clay mineral containing soils. The pesticides are used as nematocides\(^20\), herbicides, fungicides and insecticides. Organic molecules such as nicotine, D.D.T., Aldrin, thiocarbamate etc. find an important application as insecticides. Soil fumigants
such as methyl bromide, 1,3-dibromopropene, 1,2-dichloropropane and telone are widely used in the control of nematodes, root-rot fungi and weed growth.

On application to soils the pesticides may be adsorbed on the clay substrate, undergo an exchange with cations or anions of the clays, cause a variation in the nutrient availability and microorganisms of the soil and bring about various physico-chemical changes in the clays and soils. Adsorption of organic compounds on clay surfaces depends upon several factors, such as strong cation dipole attractions, hydrogen bonding, solvation of cations by polar molecules, coordination, cation exchange reactions, van der Waals interactions, pH and other environmental conditions.

Clay minerals constitute the most important reactive surfaces of the soil. They have been reported to provide heterogeneous chemical spots in the form of sorbed water around cations, hydroxyls at the edges, lattice surface oxygens and electrical double layer of changing polarity at the edges. They possess electron accepting sites in form of exposed aluminium and transition metals in higher valency state at the edges. The location and distribution of exchange sites on clays is an important factor in the nature and extent of adsorption.

Clays occur widely as the colloidal constituent of soils. Inspite of their being the most reactive fraction of soils, relatively little data exist on the mechanism of interactions between the pesticides in solution and the surface phase of these minerals. Because of the existence of exchangeable cations at these interfaces
clay minerals on dispersion in solution exhibit an exchange potential and may form important exchangeable phases for some pesticides like nicotine, zinc compounds etc.

The effectiveness and availability of a pesticide in soil depends upon a large number of factors such as mechanism of adsorption on clay and soil surfaces, mechanism of exchange on clay and soil surfaces, soil microorganisms and pH, clay mineral composition etc.

The phenomena of adsorption and exchange increase the persistence and check up the movement and degradation of pesticides. It also sometimes renders them inactive and may lead to physico-chemical changes including nutrient availability to plants. There is some lack of information on soil pesticide interactions.

In view of the great importance of such effects in soils and clays, the widespread use of pesticidal chemicals and trace metals in modern crop production and the desirability of learning as much as possible concerning their behaviour in soils after their application it was considered that studies could be usefully undertaken on clay pesticide interactions with the help of exchange adsorption isotherms potentiometric studies, thermodynamic parameters, surface activity coefficients, chemical kinetics and physico-chemical and nutrient studies.

In the studies reported hereunder nicotine was selected as the organic pesticide for fundamental studies with clays. Zinc which is an important trace metal and whose compounds find important applications as pesticides was selected as the inorganic cation for
further fundamental investigations on clays. D-D mixture formed the organic chemical for applied investigations on two selected Indian soils. The interactions were examined from several angles and reaction mechanisms worked out with clays of diverse groups wherever necessary.

Soil fumigation is widely used in modern agricultural practice to obtain high yield of crops. Considerable work has been done in the field of nematode and fungal disease control with chloride and bromide containing fumigants^{26,27} since around the first of the century. Workers^{28,29} have reported varied physical, chemical and biological changes brought about by fumigants in soils. Work on the major nutrient availability in presence of pesticides has been reported by Irsen^{30}, Castro^{31}, Wadding et al.^{32}, Alexander^{33}, Thiexe^{34}, Koike^{35}, Smith^{36} and others^{37}. Marked alterations in the activity and population of micro-organisms, acceleration and retardation in nitrification of ammonium nitrogen, increased availability of phosphorus and leachability of potassium are some of the reported results^{38}. There have been variations in effects with lapse of time. Some of the conclusions drawn have been contradictory.

D.D. is a mixture of 1,2-dichloropropene and 1,3-dichloropropene. It is an important nematocide and is extensively used for this purpose. The use of such chlorinated chemicals is finding increasing application in agriculture. Since it is possible that these pesticides may effect nutrient availability in soils and bring about other transformations, it is useful to examine the influence of this fumigant on nitrogen, phosphorus and potassium availability in a few selected
Indian soils. The effect of passage of time on some of these aspects is also worth examining. In view of the likely indiscriminate use of pesticidal chemicals in modern crop production, such studies can provide interesting results.

The subject matter of the thesis was investigated on the following lines:

(i) Adsorption of nicotine with hydrogen and sodium saturated dickites.

(ii) Adsorption and reactions of zinc with hydrogen and sodium saturated dickites.

(iii) Studies on the thermodynamics of exchange of nicotine with Al-montmorillonite.

(iv) Studies on the thermodynamics of zinc exchange with montmorillonite.

(v) Studies on the kinetics of zinc exchange with Na-dickite.

(vi) Studies on the influence of a pesticide (D-P mixture) on some nutrients of soils.

A brief account of the results achieved on the basis of the plan mentioned above is presented below:

**ADSORPTION OF NICOTINE WITH DICKITES**

In the first instance the adsorption of nicotine with hydrogen and sodium saturated dickites was examined. According to the results obtained the adsorption of nicotine on acid and base saturated dickites yielded cation dependent adsorption isotherms similar to class "H" and "L" respectively. The pH, electrical
conductivity changes and adsorption pointed to initial coordination of the nicotine molecule with H-dickite followed by interaction with the 'Lewis' acid sites at the edges. Adsorption of nicotine on Na-dickite, on the other hand, was weak and mainly due to hydrogen bonding, followed by chemisorption at the edges. X-ray diffraction provided evidence that only edge sites were involved in the reaction.

**Absorption and Reactions of Zinc with Anhydrous and Sodiumpy Saturated Dickites**

In this part of the study, the effect of pH, time, and temperature on the interaction of zinc with acid and basic saturated dickites was investigated. Increase in pH resulted in an increase in adsorption of zinc in the higher concentration range. The adsorption increased rapidly and then slowly with increase in the time of interaction. The variation of rate constants and the half times of reaction suggested an exchange process controlled by film and possibly particle diffusion and thereafter fixation processes. The inferences found support from the nature of adsorption isotherms. Temperature affected adsorption with exothermic interactions. The activation energy of adsorption of zinc on Na-dickite was 14.0 Kcal mole⁻¹.

**Studies on the Thermodynamics of Exchange of Nicotine with Al-Montmorillonite**

The interaction of nicotine on Al-montmorillonite was examined on the basis of Gaines and Thomas model of thermodynamic treatment in which the ion exchange equilibria involving the
interaction of nicotine with Al-montmorillonite was studied. The exchange isotherms, both at 30° and 60°C indicated a preference for aluminium ions by montmorillonite as compared to nicotineum ions. Separation factor supported the conclusion. Enthalpy gain was indicative of a tighter binding of aluminium. Entropy gain was indicative of a diffused and disordered arrangement of nicotineum ions in the Goüy layer with aluminium forming a more ordered arrangement in the Stern layer.

STUDIES ON THE THERMODYNAMICS OF ZINC INTERA CTION WITH MONTMORILLONITE

In this part of the study the ion exchange equilibria and mechanism of zinc exchange with sodium montmorillonite was studied with the help of adsorption isotherms and thermodynamic parameters. The exchange isotherms, $K$ and $\Delta G^0$ values indicated a spontaneity of reaction and a higher preference of zinc for the montmorillonite surface. A stronger binding of zinc and changes in the hydration rates of zinc and sodium with increase in order was suggested by enthalpy and entropy effects respectively. The surface phase activity coefficients and the excess thermodynamic functions were indicative of a nonideal heterogeneous exchange in which the mixture of zinc and sodium ions on the montmorillonite surface was more stable and more tightly bound with significant differences in the hydration rates of the ions in the mixture with respect to the homo-ionic forms.

STUDIES ON THE KINETICS OF ZINC EXCHANGE WITH Mg-DICLITE

A kinetic approach to ion exchange equilibria involving
inorganic ions on clays has recently gained considerable importance. Investigations in this chapter are based on Boyd, Adamsen and Myers model in which a kinetic study was made to predict the behaviour of zinc exchange over sodium dickite. The rate determining step as revealed by the interruption and equation tests for the zinc exchange over Na-dickite was film diffusion at all the dilutions and temperatures investigated. Diffusion coefficients, half times of exchange, energies of activation and other kinetic parameters were calculated and used to predict the theoretical behaviour of the exchange.

**STUDIES ON THE INFLUENCE OF A PESTICIDE (D-D MIXTURE) ON SOME NUTRIENTS OF SOILS**

Lastly the results of fumigation of a mixture of dichloro-propene and dichloropropene on the physico-chemical characteristics and major nutrients of a black cotton soil and a saline soil were studied. In the case of black cotton soil the results of statistical analysis of the experimental data showed that while in smaller doses the fumigant significantly stimulated the availability of nitrogen and phosphorus higher doses tended to be toxic. Lower doses had a non-significant suppressive influence on potassium availability. Organic matter was significantly reduced with increasing doses of D-D mixture. In general the stimulation after reaching a maximum gradually declined. There was no marked effect on the pH and electrical conductivity. The results were explained on the basis of microbial activity. In the case of the saline sodic soil, the results were almost similar. The two diverse soils thus behaved almost similarly towards D-D mixture fumigati