PAPERS PUBLISHED AND COMMUNICATED


ADSORPTION OF TELONE ON KAOLINITE: PART 1

J. P. SINGHAL AND DINESH KUMAR

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

Received for publication January 16, 1975

ABSTRACT

A study of the adsorptive behavior of the pesticide 1,3-dichloropropene on kaolinite suspensions as affected by saturating cations yielded "H" class isotherms. Rapid initial adsorption pointed to chemisorption as a cation exchange reaction.

The data did not agree with the Langmuir equation. Adsorption in excess of cation exchange capacity suggested a possible van der Waals interaction over the chemisorbed layers. No desorption of the pesticide occurred on treatment of the complexes with inorganic salts.

There were marked pH and electrical conductivity changes during the interaction. A reaction mechanism for the chemisorption of the pesticide on acid and base saturated kaolinites has been proposed.

X-ray diffraction and IR spectroscopy supported interaction of the pesticide at the edge surface of the kaolinites.

MATERIALS AND METHODS

Kaolinite used in these studies was from Bath, South Carolina, and was a monomineralic standard of Project No. 49 of the American Petroleum Institute. Less than 2μ clay fraction was purified by sedimentation and centrifugation. The suspension was then converted into Na-clay by treatment with 2N NaCl and washing with distilled water till the conductivity of the filtrate became constant and no chloride was detected in the filtrate with silver nitrate solution. For the preparation of the hydrogen-saturated clay (Aldrich and Buchanan 1958) the Na-clay suspension was passed through a column of H-Dowex-50W-X8 cation exchange resin just prior to use, until the conductance and pH of the suspension became constant. The concentration of Na- and H-clay suspensions was 1.10 g of clay per 100 ml of suspension.

Adsorption experiments were done by placing 10.0 ml of the clay suspension in each case, in a number of glass-stoppered tubes and adding varying amounts of an alcoholic solution of telone (10 g/liter) and adjusting the mixture to constant volume with conductivity water. The tubes were shaken for 6 hr on each day for 3 days at 30° ± 1°C to attain equilibrium. The mixtures were then allowed to sediment overnight. Then their pH and EC were recorded. The supernatant liquids taken out, centrifuged, and...
then refluxed with normal alcoholic KOH. The pesticide was estimated as halide as per Volhardt's silver thiocyanate-ferric alum method (Scott 1939). All estimations were run in duplicate and clay blank included in each case. The adsorption of telone was obtained from the change in concentration of the solution before and after contact with clay. Adsorption isotherms were plotted between equilibrium concentration of the suspension and mmoles of telone adsorbed per 100 g clay (Fig. 1). The results of the pH and conductivity variations are represented in Figs. 2 and 3.

Desorption of the telone from the clays was attempted in all cases, with deionized water and with varying concentrations of KNO₃ kept in contact with the complexed clay suspensions for 3 days. Concentrations of KNO₃ up to seven times the base exchange capacity of the clay and repeated washing with deionized water did not desorb the pesticide from the clay surface.

The BEC of the clay determined as per Ganguli's method (1951) was 8.42 me/100 g clay.

An attempt was made to correlate the adsorption data with x-ray diffraction. The x-ray analysis was done on acid and base saturated samples of kaolinite, on samples treated with telone and with glycerine. For x-ray analysis the samples were oriented on glass microslides from water suspensions at room temperature. Patterns were recorded after air-drying and after heat treatment of the samples at 550°C for 1 hr, using filtered Cu Kα radiation on a Philips diffraction unit at a speed of 2° 2θ/min. Basal spacings in angstroms deduced from the positions of 001 reflections are given in Table 1.

For a further study of the mechanism of

![Fig. 1. Adsorption isotherms of telone on sodium- and hydrogen-saturated kaolinite clays.](image-url)
interaction the acid-, sodium-, and telone-saturated clays were subjected to infrared analysis on a Beckman IR-20 double beam spectrophotometer in the range of 4000-250 cm⁻¹.

RESULTS AND DISCUSSION

Adsorption of 1,3-dichloropropene (telone) on H- and Na-saturated kaolinite suspensions (1.1 percent wt/vol) in the equilibrium concentration range of 0 to 1.8 mmoles of telone per liter yielded isotherms (Fig. 1). An examination of the adsorption isotherms revealed that they were similar to class "H" isotherms as defined by Giles et al. (1960). The initial part was vertical indicating that telone had a very high initial affinity for the clay systems with the result that in dilute suspensions it was completely adsorbed, producing steeply rising curves. This happened up to an adsorption value of 16.4 mmoles of telone per 100 g and a pH value of 3.5 in the case of H-saturated clay and a value of 9.8 mmoles of telone per 100 g and a pH value of 3.7 in the case of the Na-saturated kaolinite. This region was, therefore, indicative of the chemisorption of the nematocide on the external surfaces (Huang and Liao 1970) of kaolinites. Thereafter a change of slope occurred in the adsorption isotherms; the curves became sigmoid, showing both positive and negative adsorption. The small amount of negative adsorption with fluctuations in the isotherms, especially in the case of the Na-clay, seemed to be due to a change from a hydrophobic to a hydrophilic nature of the clay resulting in preferential adsorption of the solvent (H₂O) and release of telone. Such effects during clay-organic interactions have been observed elsewhere also (Kalb and Curry 1969). Thereafter the adsorption of telone continued to rise until values of 40.0 and 25.0 mmoles per 100 g of H- and Na-clays were reached, respectively.

In spite of the greater deflocculation effect and larger surface area exposed by Na-clays in comparison to H-clays for adsorption a greater amount of telone was adsorbed by the acid clay than by the Na-clay. The nature of exchangeable cation thus seemed to determine the extent of adsorption. The order of adsorption found confirmation (Bailey et al. 1968) from the partial molar free energy changes that occurred

![Figure 2](image-url)
during the interaction. The changes in partial molar free energy $F$ were calculated from the thermodynamic relationship: 
\[ -F = RT \ln \frac{C_e}{C_0} \]
where $C_e$ and $C_0$ were the equilibrium and initial concentration of the suspension, respectively. An average of four values of $F$ in the case of H- and Na-saturated kaolinites yielded 520.8 and 413.2 cal/mol, respectively, thus confirming the extent of the driving force available for the adsorption of telone on the kaolinites. The order of adsorption indicated that a greater amount of pesticide will be needed for application as an optimum dose in acidic kaolinitic soils than in alkaline kaolinitic ones.

The "H" nature of adsorption isotherms suggested a multilayer adsorption of the chemical or adsorption occurring at different spots with different energy levels on the clay surface. Adsorption occurring much in excess of the base exchange capacity, however, pointed to formation of multimolecular layers of telone on the clay surface. An attempt to fit the data in the

![Graph](image)

**Fig. 3.** Variation in electrical conductivity of sodium- and hydrogen-saturated kaolinite clays with amount of telone adsorbed.

**TABLE 1**

<table>
<thead>
<tr>
<th>Nature of kaolinite</th>
<th>Basal spacings at 001 reflections in angstroms</th>
<th>Interlayer separation in angstroms</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-treated kaolinite</td>
<td>7.051 (S)*</td>
<td>—</td>
</tr>
<tr>
<td>Telone-treated H-kaolinite</td>
<td>7.1820 (W)*</td>
<td>0.0569</td>
</tr>
<tr>
<td>Na-treated kaolinite</td>
<td>7.0182 (S)</td>
<td>—</td>
</tr>
<tr>
<td>Telone-treated Na-kaolinite</td>
<td>7.1897 (M)*</td>
<td>0.1705</td>
</tr>
<tr>
<td>Telone complex treated with glycerine</td>
<td>7.2484 (W)</td>
<td>0.0505</td>
</tr>
<tr>
<td>Na-treated kaolinite at 550°C</td>
<td>Collapsed</td>
<td>—</td>
</tr>
<tr>
<td>Telone-treated Na-kaolinite at 550°C</td>
<td>Collapsed</td>
<td>—</td>
</tr>
</tbody>
</table>

* S - strong, M - medium, and W - weak
Langmuir equation \( (C/x/m) = (1/KB) + (C/B) \)

where \( C \) is the equilibrium concentration of telone, \( x/m \) the amount adsorbed, and \( K \) and \( B \) the constants, did not yield a straight line plot which agreed with the stipulation of multi-molecular adsorption. These considerations (Moore 1962), along with the initial rapid adsorption, suggested formation of chemically sorbed layers of telone overlain by probable physically adsorbed layers due to van der Waals forces.

The adsorption of telone was very strong since no desorption occurred by repeated treatments with potassium chloride and washing with deionised water. Although there is evidence that organic molecules bound to clay surfaces by van der Waals forces may not be readily removed by extraction with solutions of neutral salts, the strength of binding suggested that a substantial part of telone was bound to the edge surfaces by irreversible chemisorption.

Schofield and Samson (1954) and a few other workers (Fordham 1973) have reported creation of a positive electrical double layer due to exposed alumina sheet or broken silica surface at the edges of kaolinite at lower pH. Such spots may also be in the form of \( H^+ \) and \( Na^+ \) on the edges and corners of acid and base saturated kaolinites.

When added to deionized water the pesticide showed a fall in pH from 6.0 to 2.5 and a rise in electrical conductivity from \((0.1 \times 10^{-4}) \) to \((11.0 \times 10^{-4}) \) mhos cm \(^{-1}\). In aqueous medium it thus underwent hydrolysis and protonation according to the equation:

\[
\begin{align*}
\text{Cl} & \text{C=CH—CH}—\text{C}—\text{H} & + H_2O \rightarrow \\
\text{H} & \text{C}=\text{CH—CH}—\text{OH} & + HCl \\
\end{align*}
\]

The allyl cation could be represented as a resonance hybrid

\[
\begin{align*}
\text{Cl} & \text{C=CH—CH}—\text{C}—\text{H} & \rightarrow \\
\text{H} & \text{C}=\text{CH—CH}—\text{OH} & + HCl
\end{align*}
\]

The addition of telone to the clays produced variations in pH and electrical conductivity of the equilibrium suspensions as shown in Figs. 2 and 3, respectively. Significantly, inflections occurred both in the pH and electrical conductivity curves at the same points at which there was a change in the trend of adsorption. The decrease in pH and a rise in electrical conductivity were highly significant and furnished a very powerful clue as to the mechanism of chemisorption of the pesticide on the kaolinite surface. An examination of the structure of the nematocide molecule revealed that the chlorine bound to the methylene group, being allylic, was more easily replaceable than the vinylic chlorine. The reaction of H-saturated kaolinite with 1,3-dichloropropene can, therefore, be represented by the equation:

\[
\begin{align*}
\text{Cl} & \text{C=CH—CH}—\text{C}—\text{H} & + H^+ \text{clay}^* \rightarrow \\
\text{H} & \text{C}=\text{CH—C}^+\text{H}—\text{O} & + HCl
\end{align*}
\]
Acrolein by an interaction with $H^\ominus$ clay$^\ominus$ resulted in the formation of an intermediate as shown in Eq. (7).

This resulted in the adsorption of the pesticide on Na-kaolinite. Production of HCl during the interaction resulted in a decrease of pH and a rise in electrical conductivity. The difference in the nature of the interaction of the pesticide with H- and Na-kaolinites was responsible for the difference in the order of adsorption observed in the case of acid and base saturated clays.

Examination of the kaolinite-telone complexes under x-ray diffraction did not yield any marked increase in basal spacing (Table 1). Treatment of the complex with glycerine showed no marked variation. Heat treatment at 550°C resulted in a complete collapse of the kaolinite peaks. These observations were in line with the fact that no planar space was available in kaolinite for the interaction with telone and only the edge cations took part in the reaction with telone.

A study of infrared spectra of the H- and Na-kaolinites and their telone complexes revealed only a change in the intensity of absorption. Definite frequency changes and telone peaks were not visible in the IR spectra of the complexes. Since only edge adsorption occurred on the kaolinite surfaces, the amount of adsorbed telone probably was not enough to produce visible changes in the IR spectra. This versatile tool, therefore, could not throw further light on the mechanism of the interaction.

ACKNOWLEDGMENT

Thanks are due to M. S. Ahmad and Abrar Mustafa Khan for helpful suggestions.

REFERENCES


STUDIES ON ADSORPTION

III. Adsorption of Telone on Illites

J. P. Singhal and Dinesh Kumar

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

Received December 25, 1975

The interaction between Telone, a pesticide, 1,3-dichloropropene, and acid- and base-saturated illites has been studied with the help of adsorption isotherms, desorption, pH, electrical conductivity, X-ray, and infrared spectra. The results furnished adsorption isotherms with three clearly defined portions: an 'H' curve, a 'C' curve, and a subsequent 'H' portion. The curves represented a process of chemisorption of the nematocide followed by slow penetration of the substrate micropores by the solute at the planes, edges, and corners of illite structure. The results were in accordance with the existence of three 'sites' of different reactivities on the illite surface. A reaction mechanism for the process of chemisorption has been proposed.

Clays form complexes with organic compounds of varying stabilities and properties (10). Such interactions are of great importance in the industrial and agricultural fields. The binding, persistence, chemical and biodegradation, leachability and translocation of pesticides in soils depend upon these interactions. The insecticides, nematocides, herbicides and fungicides may be rendered inactive by adsorption or their toxicities reduced by catalytic degradation at the clay surface, or, where conditions have changed, be rendered active again. Excellent studies on the adsorption of pesticides have been made by Bailey (2), Nearpass (11), Weber (14), and others.

Telone® (1,3-dichloropropene, \( \text{Cl} > \text{H} \text{C}=\text{CH} - \text{CH}_2 - \text{Cl} \)) is an important pesticide which is extensively used for the control of nematode and fungus diseases (13) in soils. Illite is an important clay mineral occurring in argillaceous sediments found on a large scale in India and other parts of the world. The mineral has been found to possess reactive sites at the edges, corners, interlayer, and interlattice positions (8, 9). While the nematocidal action of Telone in soils has been extensively investigated, fundamental studies on its mechanism of adsorption on illite are lacking.

It was, therefore, considered that studies on the mechanism of interaction of Telone with illite in its acid- and base-saturated forms in dilute suspensions with the help of adsorption isotherms, pH and electrical conductivity changes will be significant to our knowledge of the reactions of organic compounds in clays and soils.
MATERIALS AND METHODS

The work described in this paper was carried out with <2μ fraction of illite from Morris, Illinois (A.P.I. sample obtained from Ward's Natural Science Establishment, Inc.). It was converted into chloride-free Na- and H-saturated suspensions with a constant pH and electrical conductivity (vide ALDRICH and BUCHANAN (1)). The concentration of the suspensions was 12.5 g/liter in both cases. The BEC of the illite determined as per GANGULI's method (3) was 24 me per 100 g clay.

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 (0.1 to 2.5 ml) of an alcoholic solution of Telone (conc., 10 g/liter). The mixtures were diluted to 25 ml with alcohol and water so that the alcohol content of the suspension was minimum and same (2.5 ml) in all cases. After intermittent shaking and standing for 72 hr, the suspensions were centrifuged, and their pH and electrical conductivity recorded. The suspensions were then centrifuged. The supernatants showed the formation of chloride. There was also residual Telone in them. Since refluxing with KOH is necessary to decompose Telone and estimate it by Volhard's method, the chloride ions and the residual Telone, if any, were estimated separately in the supernatants with and without refluxing the supernatants with N alcoholic KOH by Volhard's silver thiocyanate ferric alum method (12). The difference gave the amount of Telone and chloride in the equilibrium liquids after adsorption. All estimations were run in duplicate and blanks included. The amount of Telone adsorbed was determined as the difference between the amount of Telone added and remaining after contact with the clay. Adsorption, pH, and conductivity curves were plotted (vide Figs. 1–3.

Attempted desorption of Telone from the H- and Na-illites with KNO₃ solutions, added up to five times the BEC, did not result in release of the organic chemical from the illites.

The adsorption was also examined with the help of X-ray diffraction. For X-ray analysis less than 2 μ H- and Na-saturated illite samples were taken along with the samples complexed with 1.8 mmoles of Telone per g clay. They were carefully oriented on micro glass slides. Patterns were obtained using filtered CuKα radiation on a Philips diffraction unit at a speed of 2 degrees 2θ per min with the air dry samples, with Telone-complexed samples, with glycerine-treated complexed samples and with complexed samples after heat treatment at 550°C. Basal spacings in Å are given in Table 1.

The samples were also subjected to infrared analysis using the KBr pellet technique on a Beckman IR-20 double-beam spectrophotometer in the range 4000–250 cm⁻¹.

RESULTS AND DISCUSSION

A plot of the results of adsorption of Telone on H- and Na-saturated illites in dilute suspensions (1.25%, w/v) in the equilibrium concentration range of 0 to 2.5 mmoles of
Adsorption of Telone on Illites

Table 1. Basal spacing of H-, Na-, Telone, glycerine- and heat-treated samples of illite.

<table>
<thead>
<tr>
<th>Nature of illite</th>
<th>Basal spacings at 001 reflections in Å</th>
<th>Interlamellar separation in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-illite air dry</td>
<td>10.15</td>
<td>—</td>
</tr>
<tr>
<td>H-illite Telone complex</td>
<td>10.15</td>
<td>—</td>
</tr>
<tr>
<td>H-illite Telone complex treated with glycerine</td>
<td>9.93</td>
<td>—0.22</td>
</tr>
<tr>
<td>H-illite Telone complex at 550°C</td>
<td>10.04</td>
<td>—0.11</td>
</tr>
<tr>
<td>Na-illite air dry</td>
<td>10.04</td>
<td>—1.1</td>
</tr>
<tr>
<td>Na-illite Telone complex</td>
<td>10.15</td>
<td>0.11</td>
</tr>
<tr>
<td>Na-illite Telone complex treated with glycerine</td>
<td>9.93</td>
<td>—0.11</td>
</tr>
<tr>
<td>Na-illite Telone complex at 550°C</td>
<td>10.04</td>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 1. Adsorption of Telone on Na- and H-saturated illites (●, hydrogen illite; ○, sodium illite)

the pesticide per liter yielded isotherms (Fig. 1). The isotherms exhibited three positive regions of adsorption and were similar to class ‘H’ and ‘C’ isotherms as defined by Giles et al. (4). In the initial stages the pesticide had such a high affinity for the illites that in dilute suspensions it was completely adsorbed so that there was no measurable amount left in solution. This part of the isotherm was, therefore, vertical and here adsorption occurred up to 28 and 20 m moles of Telone per 100 g of H- and Na-saturated illites and up to a pH value of 2.8 and 7.0 respectively. Adsorption up to this limiting
The value was in the neighbourhood of the base exchange capacity of the clays. The iso-
therms then changed their slope to a linear rise till adsorptive values of 80 and 70 mmoles
of Telone per 100 g of H- and Na-illite, respectively were reached with a further fall in
pH values and a rise in E.C. As these surfaces were saturated one after another a third
region of another steep rise occurred in the adsorption isotherms. Thus it was clear that
in both the cases, the curves consisted of three clearly defined portions: first the ‘H’
(high affinity) curve, with a flat plateau, next a ‘C’ (linear rising) curve, then another
‘H’ portion. The last mentioned section was beginning to change to a plateau, in the
case of the Na-material, but had not yet done so in the case of H-illite.

The ‘H’ sections of these curves certainly represented some form of chemisorption
occurring at the outer surfaces of illites with edge to edge ion attraction (6, 7). The
second region, as represented by the linear intermediate section of the curves, indicated
creation of new adsorption sites in the substrate with slow penetration (5) of the solute
in its micropores. As these sites were filled up, another process of chemisorption occurred
as revealed by the subsequent ‘H’ curve. The results thus pointed to an interaction of
Telone at three different ‘sites’ of illite associated with different energy levels. Existence
of such ‘sites’ with diverse reactivities on illite surface have been reported by earlier
workers in these laboratories (8) and elsewhere (9).

Attempt to desorb Telone from the acid- and base-saturated illites with potassium
salts and repeated washings with deionized water did not prove successful suggesting
that the pesticide was strongly bound to the illite surfaces by electrostatic forces. There
is evidence that organic molecules bound to clay surfaces in the fine pores and cavities
may not be removed by extraction with solutions of neutral salts, which accounts for the
irreversibility of the stipulated adsorption.

![Graph](image-url)
AdSORPTION OF TElONE ON ILLITES

477

Fig. 3. Variation in electrical conductivity of Na- and H-saturated illites with amount of Telone adsorbed (●, hydrogen illite; ○, sodium illite)

In spite of the greater deflocculation effect and larger surface area exposed by Na-illite, a greater amount of Telone was adsorbed by H-illite in the initial and final stages. The nature of cation thus determined the extent of Telone adsorption on illites.

A careful record of the pH and electrical conductivity changes as compared to the blank yielded curves (Figs. 2 and 3). In general these curves showed sharp changes at almost the same points at which there was a change in the trend of adsorption. The sharp fall in pH (3.5 to 2.5 in H-illite and 7.8 to 2.8 in Na-illite) and a rise in electrical conductivity (0.9 to 4.7 × 10⁻⁴ mho cm⁻¹ in H-illite and 0.4 to 3.9 mho cm⁻¹ in Na-illite) were highly significant and provided a powerful clue as to the mechanism of chemisorption of Telone on illites. Our pesticide ClH > C=CH—CH₂—Cl was an unsaturated cationic molecule with one chlorine bound in allylic position and the other in vinylic position. The methylene group being allylic could be more easily replaced in cation exchange reactions than the vinylic chlorine. Thus the H-illite could be acted upon by Telone as follows:

ClH > C=CH—CH₂—Cl + H⁺ illiteΩ → ClH > C=CH—C⁺ H₂ illiteΩ + HCl

The formation of HCl was in accordance with the pH and electrical conductivity changes observed during the interaction (Figs. 2 and 3).

A direct cation exchange reaction of the above type, represented by Eq. 2 in the case of Na-illite could not, however, explain the pH and electrical changes that occurred during this interaction.

ClH > C=CH—CH₂—Cl + Na⁺ illiteΩ → ClH > C=CH—C⁺ H₂ illiteΩ + NaCl

In this case a reaction mechanism with the intermediate steps shown below is, therefore, proposed. The allyl cation could be represented as a resonance hybrid.
The cationic intermediate appeared to react with a molecule of water in the dilute suspension releasing a proton and giving α-chlorohydrin, the latter being unstable dissociated into HCl and acrolein (Eqs. 4 and 5).

Acrolein by an interaction with H\textsuperscript{+}illite\textsuperscript{−} formed an intermediate as shown in Eq. 6.

This caused the adsorption of the pesticide on Na-illite. Formation of HCl during the reaction resulted in a sharp fall in pH and a rise in electrical conductivity. The difference in adsorption observed in the case of H- and Na-illites was due to a difference in the nature of reaction mechanism in the two cases.

That the interaction of Telone mainly occurred at the external basal surfaces and edges and corners of illites found support from X-ray analysis of the complexes. Only a minor expansion (Table 1) occurred in the basal thickness of Na-illite on treatment with Telone. Glycerine treatment too did not cause further expansion. Heat treatment was generally without effect on basal thickness. These results showed that only the external basal surfaces and the lateral edge and corner sites of illites were available for interaction with Telone.

The samples were also examined with infrared spectroscopy using KBr pellet technique. This versatile tool, however, did not reveal any marked changes in frequency or in the position of Telone peaks in the infrared spectra of the complexes which was probably due to the small concentration of the complexes in the suspensions and the difficulty in obtaining self supporting clay-organic films for infrared examination.

Acknowledgment. Thanks are due to Prof. M. S. Ahmad for helpful suggestions and Prof. Mohsin Qureishi for laboratory facilities.
REFERENCES

THERMODYNAMICS OF EXCHANGE OF ZINC WITH Mg-BENTONITE AND Mg-ILLITE

J.P. SINGHAL and DINESH KUMAR

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

(Received March 18, 1976; accepted November 11, 1976)

ABSTRACT


The ion-exchange equilibria of Zn with Mg-bentonite and Mg-illite have been studied with the use of exchange isotherms and thermodynamic parameters. The exchange isotherms and the equilibrium constants point to a lower preference for Zn than Mg ions by both clays. Preference differed with temperature. Free energy changes were in agreement with this conclusion. Positive enthalpy and entropy changes occurred during Zn exchange with bentonite, whereas the reverse was the case with illite. These changes indicate diversity in the strength of binding and order of distribution of Zn ions on surfaces of the two clays.

INTRODUCTION

Base exchange in clays and soils is an important phenomenon. Consequently, it has been under serious investigation since the beginning of the present century. As early as 1913 Gans (1913) and later Kerr (1928) applied the mass-action law in ion-exchange studies. Later, Vanselow (1932) and Krishnamoorthy and Overstreet (1949) all tried in their own ways to obtain equilibrium constants for exchange of metal ions in soils. It was, however, only during the second half of the current century that this phenomenon received rigorous thermodynamic treatment (Gaines and Thomas, 1953; Howery and Thomas, 1965; Singhal and Singh, 1973).

In view of the activity of Zn as a trace element and as a pesticide in the soil solution nourishing plant roots, the aim of the present work was to study the exchange of Zn with two important types of clay saturated with magnesium. Reliance was placed on thermodynamic models of earlier workers and more recent studies by Singhal et al. (1976 a, b).

MATERIALS AND METHODS

The clay minerals used in these studies consisted of bentonite from
Polkville, Mississippi and illite from Morris, Illinois. Both samples were monomineralic standards of the American Petroleum Institute, verified under the direction of Dr. Ralph J. Holmes of Columbia University. Samples were obtained from Ward's Natural Science Establishment, Inc. X-ray analysis of the <2µ fraction showed that montmorillonite and illite, respectively, were the main constituents of the clays. The ammonium acetate method of Jackson (1958) yielded cation exchange capacity (CEC) values of 90 and 30 mequiv. per 100 g, respectively for the two clays.

After removal of organic matter the clays were dispersed with 2M NaCl and then centrifuged to give suspensions of <2µ particles. The NaCl treatment was repeated twice and the suspensions freed from chloride ions by washing with water. The Mg-bentonite and the Mg-illite suspensions were prepared from the Na-clays by saturating them with N MgCl₂ and washing to remove excess salt. The concentrations of the suspensions, as determined by evaporation, were 7.0 g and 9.0 g per litre, respectively.

Conversion of the clays to Mg-saturated forms resulted in a reduction in the values of cation exchange capacity of the clays. The Mg-CEC values of the bentonite and illite clays were determined by treatment of the Mg-saturated clay suspensions with an acid salt mixture (0.1N HCl and 1N NaCl) and then estimating the amount of Mg released by the clays (Frink and Peech, 1963). The values came out to be 72 and 23 mequiv. per 100 g, respectively.

For the exchange experiments the pH of the suspensions was adjusted to 4.0 with dil. HNO₃ (Singhal et al., 1975). 10 ml samples of each of Mg-bentonite and Mg-illite were then placed in glass-stoppered tubes and treated with different amounts of a 0.03N Zn(NO₃)₂ solution. The volume of the mixture was adjusted to 25 ml with deionized water in each case. Each mixture was shaken for six hours at 30 ± 0.1°C in the first set of experiments and at 60 ± 0.1°C in the second set of experiments, in a water bath at constant temperature. The suspensions were then centrifuged and Mg and Zn estimated by atomic absorption in the supernatant liquids. The corresponding concentrations of Mg in the solid clay phases were obtained by substraction of the Mg concentrations in the supematants from the Mg-CEC. Similarly, the amounts of Zn taken up by the clay surfaces in replacing Mg were obtained by difference between the amounts of Zn added and the amounts of Zn remaining in the equilibrium suspensions.

RESULTS AND DISCUSSION

The exchange reaction between the Zn ions in solution and Mg ions on the bentonite and illite surfaces can be represented by the equation:

\[ \text{Mg}^{+} + \text{Zn}^{2+} \rightleftharpoons \text{Mg}^{2+} + \text{Zn}^{+} \]  \hspace{1cm} (1)

The overscored symbols represent the equivalent concentrations of the ions in the clay phase and other symbols the electrolyte concentrations in solution.
The concentrations of the ions could be represented as equivalent ionic fractions. The equivalent ionic fractions of Zn and Mg in the bentonite and illite phases and in the solutions were calculated from the following expressions:

\[
X_{Zn}^Zn = \frac{C_{Zn}}{\bar{C}}, \quad X_{Zn}^Mg = \frac{C_{Zn}}{\bar{C}}, \quad X_{Mg}^Zn = \frac{C_{Mg}}{\bar{C}} \quad \text{and} \quad X_{Mg}^Mg = \frac{C_{Mg}}{C}
\]

where \(\bar{C}\) represents the total electrolyte concentration in the clay phase and \(C\) that in the solution. The values obtained for the equivalent ionic fractions at 30° and 60°C for the two clays are represented in Fig.1.

The plots (Fig.1, 4 curves) for Zn exchange with Mg-clays showed that the isotherms deviated to the same side of the diagonal except in the case of Zn exchange with Mg-bentonite at 60°C. Thus, in both clays, Zn ions did replace some Mg ions, but preference of the minerals was lower for Zn than for Mg, except for a minor reversal at 60°C during the exchange with Mg-bentonite (Fig.1). The preference for Zn also differed with temperature, being higher

![Fig.1. Exchange isotherms of zinc on Mg-bentonite and Mg-illite at different temperatures.](image-url)
at 60°C in bentonite and at 30°C in illite. From the isotherms it also followed that the order of preference for Zn ions was, Mg-bentonite > Mg-illite at both temperatures.

To study further the exchange behaviour in the dilute clay suspensions, the selectivity coefficients were calculated by taking activity coefficients as unity (Robinson and Stokes, 1959) and using the expression:

$$K_C = \frac{X_{Zn}^Mg}{X_{Mg}^Zn}$$  \hspace{1cm} (2)

Plots of the values of log $K_C$ against $X_{Zn}$ are given in Fig.2.

For an examination of the affinity of the ions during the exchanges, the
values of an equilibrium constant $K$ were calculated by the equation (Gaines and Thomas, 1953):

$$\ln K = (Z_a - Z_b) + \int_0^1 \ln K_c \, dX_{Zn}$$

(3)

Evaluating the integral from the areas under the curves (Fig. 2) by using the trapezoidal rule, the values of $K$ were calculated and are given in Table I. The values of $K$ supported the inferences drawn from the exchange isotherms on the affinities of the ions for the clays at both temperatures.

The Gibbs free energy change for the interactions were calculated from the following equation:

$$\Delta G^\circ = -RT \ln K$$

The values obtained are given in Table I. During ion exchange for both clays, free energy changes were positive and greater for illite than bentonite. The value decreased with a rise in temperature during the exchange of Zn with Mg-bentonite but increased in the case of Mg-illite. At both temperatures the exchanges were, therefore, non-spontaneous and there was a lower preference for Zn ions, the order for Zn preference being Mg-bentonite (60°) > Mg-bentonite (30°) > Mg-illite (60°). The cation exchange of both clays thus followed the order Mg > Zn.

Enthalpy may be defined as the heat content or total energy stored in a system. It is indicative of the strength or tightness with which an ion is held on a surface and whether a reaction is exothermic or endothermic. The standard enthalpy changes $\Delta H^\circ$ during the exchanges were calculated from the Van 't Hoff equation:

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

where $T_1$ and $T_2$ were the temperatures in degrees Kelvin and $R$ the gas constant in calories per degree abs. per mole. The results are recorded in Table I.

| TABLE I |

Thermodynamic values of Zn–Mg exchange with bentonite and illite at 30°C and 60°C

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>Bentonite</th>
<th>Illite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$ (cal./mole)</td>
<td>0.748</td>
<td>0.844</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (cal./mole)</td>
<td>174.85</td>
<td>135.16</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (cal./mole)</td>
<td>796.46</td>
<td>-468.51</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (cal./mole)</td>
<td>2.05</td>
<td>-2.99</td>
</tr>
</tbody>
</table>
These values show that the reaction was endothermic during Zn exchange with Mg-bentonite and exothermic during its exchange with Mg-illite. Such energy changes indicate that Zn was less tightly bound to bentonite and more strongly bound to illite than Mg.

These conclusions are supported by the entropy gain accompanying Zn exchange with Mg-bentonite and entropy loss during its interaction with Mg-illite. Entropy loss is indicative of a greater order and entropy gain of a greater disorder produced in a system during cation transfer. The entropy changes $\Delta S^\circ$ for the exchanges were calculated from the equation:

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

The greater disorder accompanying Zn exchange with Mg-bentonite and a greater order during its exchange with Mg-illite as indicated by entropy changes (Table I) were in agreement with the enthalpy effects which also indicate strength of binding of Zn ions on the surfaces of the two types of clay.

ACKNOWLEDGEMENT

The second author is indebted to U.G.C. (India) for the grant of a fellowship.

REFERENCES


Studies on the Adsorption of 1, 3-Dichloropropene on Some Natural, Acid and Base Saturated Soils

Soils are known to adsorb organic compounds. In this domain, adsorption of pesticides is important because it often results in phytotoxicity (Singhal & Singh 1974), water pollution etc. Adsorption isotherms, pH and electrical conductivity variations can be used to provide information on the mechanism of adsorption by a soil (Singhal & Singh 1976; Singhal & Kumar 1976a, b). Regular and discontinuous isotherms due to heterogeneities on the adsorbent surface have been observed (Singhal & Singh 1974). The aim of the present work was to determine the extent and mechanism of adsorption and interaction of 1,3-dichloropropene (Telone, a nematocide) by a group of Indian soils of diverse properties.

Surface samples of the following three Indian soils with different properties were selected for the study: (I) Black soil from Kota, Rajasthan, formed by weathering of metamorphic rocks, with pH 8.0 and CEC 34.4 m.e./100g of soil. It was a dark grey montmorillonitic clay loam, belonging to Vertisols. (II) Central lowlands alluvial soil from Aligarh, Uttar Pradesh, with pH 9.5 and CEC 10.8 m.e./100g of soil. It was a solonetz, loam, illitic belonging to Aridisols. (III) Red soil from Kanke, Bihar, formed by weathering of granites, gneisses and schists, with pH 6.4, CEC 6.5 m.e./100g of soil. It was an acidic ferruginous red loam, kaolinitic soil, belonging to Oxisols.

The sodium and hydrogen saturated soils were prepared as per Aldrich and Buchanan (1958) method. The adsorption experiments and pH titrations were done as reported elsewhere (Singhal & Kumar 1976a, b). The results of adsorption and pH titrations of the natural, acid and base saturated soil suspensions (3 to 6.5%, wt/vol) with Telone are presented in figures 1 and 2, respectively.

Most of the adsorption isotherms exhibited discontinuities with sharp inflexions. Telone was completely adsorbed by acid saturated soils and in a few cases by base saturated systems (Fig. 1), the critical quantity of it being 11.6, 5.7 and 5.2 mmoles per 100g of acid saturated soil from Kota, Aligarh and Kanke, respectively, and 3.3 and 3.2 mmoles per 100g of base saturated black soil and Aligarh solonetz, respectively. Thereafter a change of slope occurred in the curves and the adsorption continued to rise with increase in concentration of Telone though at a decreasing rate. Such an initial behaviour was not observed in natural soils. The adsorption in all the soil systems occurred in the order: black soil > red acidic soil = Aligarh solonetz. Further in the natural, acid and base saturated systems the adsorption occurred in the order: H-soils > Na-soils > natural soils (Fig. 1). The nature of the soil and the cation in the soil along with pH thus determined the optimum nematocidal dose of Telone.

The up and down nature of the adsorption isotherms with sharp inflexions indicated a multilayer adsorption of the nematocide on the soil surfaces. This was in accordance with the CEC data of the soils. Adsorption, much in excess of the CEC, in the concentration range studied, was inconsistent with the formation of monomolecular layer. The above conclusion found confirmation (Hem Wall 1963) from the fact...
Fig. 1. Adsorption of Telone on natural, H-saturated and Na-saturated soils

Fig. 2. Variation in pH of natural, H-saturated and Na-saturated soils with amount of Telone adsorbed
that none of the results obtained in the study conformed to the Freundlich or Langmuir equations. Both chemical and physical adsorption seemed to operate during the interaction of Telone with the different soils.

The variations in pH during the adsorption of Telone indicated that, in general, as the adsorption increases, pH decreased (Fig. 2). The pH changes were most marked in natural soils followed by the base saturated systems and thereafter the acid saturated ones. The decrease in pH on addition of Telone pointed to the release of protons, due possibly to the reaction,

\[
\text{Cl} \quad > \quad \text{C}=-\text{CH}-\text{CH}_2-\text{Cl} + \text{H}-\text{Clay} \quad \rightarrow \quad \text{H} \\
\text{Cl} \quad > \quad \text{C}=-\text{CH}-\text{CH}_2-\text{clay} + \text{HCl}.
\]

The weak adsorption on sodium soils, in contrast to the strong adsorption on hydrogen saturated systems (Fig. 1) further confirmed the above interaction. A smaller number of exchange sites appeared to be occupied in the sodium system than in the hydrogen system.

From the above observations it is concluded that the primary mechanism of Telone adsorption was ion exchange and adsorption occurs in molecular form by van der Waal's forces on the soil systems.

Faculty of Engineering and Technology, Muslim University, Aligarh, Uttar Pradesh

REFERENCES


(Received: October, 1974; Accepted: May, 1976)
of the sample. Theories accounting for such behaviour have recently been summarised by Rieke and Chilingarian (1975).

Further consolidation tests on montmorillonite are currently in progress at Imperial College using the apparatus described in this paper. These tests are being conducted over a range of temperatures from 20 to 80°C.

Acknowledgements—I would like to thank M. K. Armstrong, B. A. Clarke, M. H. de Freitas and B. J. Hough for help in conducting this series of experiments and for criticism during the preparation of this paper. The research reported herein has been sponsored in part by the United States Army through its European Research Office and the author has been supported by a Natural Environmental Research Council research studentship. Both awards are gratefully acknowledged.

REFERENCES


Rieke, H. H., Chilingar, V. G. and Robertson, J. O. (1964) High pressure (up to 500,000 psi) compaction studies on various clays: 22nd Int. Geol. Cong., New Delhi 15, 22-38.


STUDIES ON ADSORPTION OF TELONE—II:

ADSORPTION OF TELONE ON MONTMORILLONITES

J. P. SINGHAL and DINESH KUMAR

Chemical Laboratories, Faculty of Engineering and Technology,

Muslim University, Aligarh, India

(Received 22 December 1975; and in final form 3 February 1976)

Abstract—The interaction of telone with acid and base saturated montmorillonite furnished adsorption isotherms which possessed combined features of H (high affinity) and C (linear rising) class isotherms; a fall in pH, an increase in electrical conductivity and formation of chloride ions. The observations were indicative of a process of chemisorption, both at the planar and lateral sites of montmorillonites, followed by penetration and swelling of the substrate micropores with telone. A reaction mechanism for the process of chemisorption has been proposed.

INTRODUCTION

The importance of a study of the retention of complex pesticidal organic chemicals by soil clays is well understood. Excellent studies on adsorption of pesticides have been made by Bailey (1971), Bailey et al. (1970), Nearpass (1965) and others.

1,3-dichloropropene, C=CH—CH₂—Cl (telone) is widely used as a nematocide (Taylor, 1951). It is a cationic molecule with one chlorine bound in allylic position and the other in vinylic position. Therefore there is a possibility of its interaction with ion exchangers. Clays provide sites for ion exchange reactions, van der Waals interactions, hydrogen bonding, strong dipole attractions, solvation of cations by polar molecules, ligand exchange and charge transfer reactions (Mortland, 1970; Bailey et al., 1968; Singhal et al., 1972). Adsorption is affected by pH, exchangeable cations, and other environmental conditions (Singhal et al., 1974). Adsorption isotherms and titration curves have been utilized by chemists to provide information on the mechanism of interaction of organics with clays. Giles et al. (1960) have classified the various shapes of adsorption isotherms with respect to the reaction mechanism concerned.

Encouraged by the earlier results on adsorption of telone by kaolinite (Singhal et al., 1976) it was considered useful to extend the investigations on the mechanism of adsorption and interaction of telone to montmorillonites.

MATERIALS AND METHODS

The montmorillonite used in these studies was from Akli (Rajasthan), India. Its mineralogical composition was verified by X-ray diffraction. A less than 2 μ fraction, obtained by repeated dispersion and centrifugation, was converted into Na- and H-saturated montmorillonites by the method of Aldrich and Buchanan (1958). Care was taken to see that it was free from chloride ions. The concentration of the suspensions was 1% in both cases.

Adsorption of telone was determined by adding different amounts of an alcoholic aqueous solution (10 g/l) of telone to 10 ml each of the appropriate clay suspension in glass stoppered tubes. An alcoholic solution had to be used due to very low solubility of telone in water. The mixtures were diluted to 25 ml with alcohol and water so that the alcohol content of the slurry was minimum and the same in all cases. After intermittent shaking and standing for 72 hr at a temperature around 30°C the pH and electrical conductance of the mixtures were recorded. The suspensions were then centrifuged. Since the supernatants showed the formation of a chloride, the chloride ions and the residual telone, if any, were estimated in the supernatants (Scott, 1939) with and without refluxing the supernatants with N alcoholic KOH. The difference gave the amount of telone remaining in the equilibrium liquids after adsorption. The amount of adsorbed telone was determined as the difference between the amount of telone added and remaining after contact with clay. The results of adsorption, the pH and conductivity variations are represented in Figs. 1-3. The BEC of the clay determined by Ganguli’s (1951) method was 90 m-equiv./100 g clay.

For the X-ray powder diffraction analysis less than 2 μ H- and Na-montmorillonite suspensions were placed on glass slides and allowed to dry to form a well oriented layer. Similar samples of H-montmorillonite-telone complex and Na-montmorillonite-telone complex with telone in excess of BEC were carefully dried and oriented on glass slides. X-ray powder diffraction patterns were recorded both with the air dry and heat treated (at 550°C for one hour) samples on a Philips diffraction unit at a speed of
Studies on adsorption of telone

The results of adsorption of telone on H- and Na-saturated montmorillonite suspensions in the equilibrium concentration range of 0 to 3.6 mmoles telone/l yielded isotherms (Fig. 1) which were similar to class H (high affinity) plus C (constant partition or linear rising) as defined by Giles et al. (1960). Although the isotherms did not coincide in the two cases, they show three clearly defined portions. First a high affinity curve with a long flat plateau up to an adsorptive value of 45 mmoles telone/100 g and a pH of 3.0 in the case of the H-saturated system and a value of 28 mmoles, a pH value of 6.8 and a short plateau in the case of the Na-montmorillonite. Second a series of high affinity curves with a second plateau in the case of H-montmorillonite only. This H section was beginning to change to a plateau in the case of the Na-material but had not yet done so. The high affinity sections of the curves almost certainly represented some form of chemisorption (Huang et al., 1970) which must be taking place in the different regions of the structure like the planar and lateral sites; the lateral site as indicated by the plateau being available after the saturation of the planar. The ending of these sections at 90 mmoles coincided with the BEC of the clay. As these sites were saturated one after another, new adsorption sites opened up due to the pressure of the adsorbate molecules beyond the exchange capacity producing the linear rising or C sections of the curves (Giles et al., 1974). These continued to well above the BEC and were due to slow penetration and swelling of the substrate micropores with telone with or without the solvent. The results were in agreement with the work of Greenland, Laby and Quirk (1962) who obtained linear isotherms for adsorption of amino acids on Ca-montmorillonite from water and were able to show by

RESULT AND DISCUSSION

The results of adsorption of telone on H and Na-saturated montmorillonite are given in Table 1.
X-ray measurements that the clay structure was steadily swelling as more solute was adsorbed.

Reversibility of adsorption was tested by repeated treatments with KNO₃ solutions added up to five times the BEC followed by washing with deionised alcoholic water. No desorption occurred. This fact along with the strong binding of the chemical was in agreement with occurrence of irreversible chemisorption and penetration in the substrate micropores.

Over quite a substantial range of equilibrium concentration a larger amount of telone was adsorbed on the Na-clay than on the H-montmorillonite. This was in agreement with the greater deflocculation effect and larger surface area exposed by the Na-clay in comparison to H-clay. The nature of the exchangeable cation thus determined the order of adsorption.

Table 1. Basal spacings of H-, Na-, telone, glycerine- and heat-treated samples of montmorillonites

<table>
<thead>
<tr>
<th>Nature of montmorillonite</th>
<th>Telone adsorbed, mmoles/g clay</th>
<th>Telone in equilibrium suspension, mmoles</th>
<th>Molecules telone/unit cell† or Å²</th>
<th>Basal spacings at (001) reflections, Å</th>
<th>Interlamellar separation, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-montmorillonite</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>9.60 (S)*</td>
<td>—</td>
</tr>
<tr>
<td>H-montmorillonite-telone complex</td>
<td>2.07</td>
<td>1.11</td>
<td>0.016</td>
<td>13.38 (S)</td>
<td>3.78</td>
</tr>
<tr>
<td>H-montmorillonite-telone complex treated with glycerine</td>
<td>2.07</td>
<td>1.11</td>
<td>0.016</td>
<td>18.02 (S)</td>
<td>8.42</td>
</tr>
<tr>
<td>H-montmorillonite-telone complex at 550°C</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>9.82 (S)</td>
<td>0.22</td>
</tr>
<tr>
<td>Na-montmorillonite</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>9.82 (S)</td>
<td>—</td>
</tr>
<tr>
<td>Na-montmorillonite-telone complex</td>
<td>1.97</td>
<td>1.03</td>
<td>0.016</td>
<td>14.72 (S)</td>
<td>4.90</td>
</tr>
<tr>
<td>Na-montmorillonite-telone complex treated with glycerine</td>
<td>1.97</td>
<td>1.03</td>
<td>0.016</td>
<td>18.39 (S)</td>
<td>8.57</td>
</tr>
<tr>
<td>Na-montmorillonite-telone complex at 550°C</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>9.82 (S)</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* S = Strong.
† Taking surface area as 760 m²/g or 760 × 10²⁰ Å²/g.
The addition of telone to the acid and base saturated montmorillonites showed pH and electrical conductivity variations as shown in Figs. 2 and 3. The curves exhibit inflexions at about the BEC of the montmorillonite. The supernatants revealed the formation of chloride ions in increasing quantities. These changes were highly significant and provided a strong evidence on the mechanism of chemisorption of the organic chemical on H- and Na-montmorillonite surfaces. The unsaturated nature of the dichloropropene molecule indicated that the methylene group being allylic could be more easily replaced than the vinylic chlorine giving a reaction with H-montmorillonite as follows:

$$\text{Cl} \quad \text{C}=\text{CH}-\text{CH}_2-\text{Cl} + \text{H}^\circ \text{mont}^\circ \rightarrow$$

This could explain the decrease in pH, a rise in electrical conductivity and formation of chloride ions during the interaction of telone with H-montmorillonite.

Such an exchange reaction does not explain the pH changes observed during the interaction of the Na-montmorillonite with telone. An explanation which could explain the interaction in this case is as follows:

$$\text{Cl} \quad \text{C}=\text{CH}-\text{CH}_2-\text{Cl} + \text{Na}^\circ \text{mont}^\circ \rightarrow$$

The allyl cation could be represented as a resonance hybrid

$$\text{Cl} \quad \text{C}=\text{CH}-\text{C}^\circ \text{H}_2 \text{mont}^\circ + \text{HCl} \quad \text{(1)}$$

This caused the adsorption of telone on Na-montmorillonite. Formation of HCl during the interaction was responsible for the decrease in pH and a rise in electrical conductivity observed during the interaction of telone with Na-montmorillonite. Confirmation of its presence as chloride in the supernatant liquids before refluxing confirmed reactions vide equations (2) and (5).

Chemisorption of telone on the planar and lateral surfaces of H- and Na-montmorillonites found support from the X-ray analysis. A reference to Table 1 indicates an interlamellar expansion of 3.78 and 4.9 Å respectively during adsorption of telone on H- and Na-clays. The stereo model structure of the pesticide yielded a van der Waals thickness of 4.62 Å in the upright state of the molecule. This thickness, along with some contraction (Greenland et al., 1965; Barrer and Reay, 1957), in the case of acid clay adsorption, and some hydration in case of Na-clay adsorption, suggests an upright monomolecular adsorption of the pesticide on the planar surface of the acid and base saturated clays. Adsorption in excess of the base exchange capacity was due to the
chemisorption of telone on the planar and lateral surfaces of montmorillonites followed by penetration of the solute into the substrate micropores. Treatment of the complex with glycerine resulted in a further expansion of basal thickness. Such an order of expansion for glycerine adsorption has been noticed by other workers (Grim, 1953) also. Heat treatment at 550°C, as expected, completely expelled the organic molecule.

Acknowledgements—Thanks are due to Prof. Mohsin Qureshi for research facilities and Prof. M. S. Ahmad for helpful suggestions.

REFERENCES


Thermodynamics of ion exchange equilibria involving Al-ions in Na- and Ca-illites

By J. P. Singhal, R. P. Singh, and D. Kumar

With 4 figures and 3 tables

Introduction

Aluminium plays an important role in soil-acidity and toxicity to plants (1). Sodium and calcium are important constituents of alkali and calcareous soils. The ion exchange reactions of aluminium have been extensively studied by several investigators (2, 3). There is an important relationship between ion exchange and plant nutrition. In the following paper, we have given a thermodynamic basis to ion exchange equilibria involving Al, Ca and Na with illite, a clay mineral which occurs widely in illitic soils. The basis of the treatment have been the thermodynamic formulations of Argersinger et al. (4), Gaines and Thomas (5), El-Sayed et al. (6), and Singhal and Singh (7). It has been felt that such a study will be of considerable interest in predicting the nature and behaviour of Al—Na and Al—Ca exchanges in illites.

Materials and methods

Illite from Morris, Illinois, was dispersed in distilled water and centrifuged. To obtain <2 µ Na-illite it was equilibrated (8) with 2 N NaCl and a small quantity of 0.1 N HCl for half on hour and the supernatant salt solution decanted. This treatment was repeated three times. The sodium illite suspension was washed free from excess salts with distilled water and alcohol until the clay dispersed and the conductivity of the aqueous suspension was of the same order as that of distilled water (10⁻⁴ mhos/cm). Calcium saturated illite was prepared from the sodium clay suspension by saturating it three times with a normal solution of CaCl₂ and then washing it as above to remove the excess salt. The base saturated suspensions were then quickly used for cation exchange experiments to avoid any ageing effects. The concentration of the suspension in both cases was 1 g/100 ml.

For the cation exchange experiments the pH of the suspensions was adjusted to 4 with diluted HNO₃ in order to provide a strong buffering action and to eliminate the possibility of hydroxide precipitation. 10 ml of the solutions and calcium illite suspensions, in each case, were quickly taken in several stoppered test tubes and various concentrations of 0.05 N AlCl₃ solution added and the mixture adjusted to constant volume with distilled water. The tubes were shaken for an hour at 25 ± 1 °C in the first set of experiments and 50 ± 1 °C in the second set of experiments in a thermostatic water bath. The mixtures were then centrifuged and the Na, Ca and Al in the supernatant liquids estimated. Na was measured flame photometrically, Ca by absorption spectrophotometry after removal of aluminium interference with 1 % EDTA; and Al colorimetrically with Bausch and Lomb spectronic 20 at 520 mu using aluminon (9) as colour reagent. The CEC value of illite was measured by the ammonium acetate method of Jackson (10). The corresponding concentrations for Na and Ca in the illite phase were obtained respectively by difference (CEC minus concentration of the cation in the supernatant liquid) and that for Al from Al added minus the cation in the supernatant liquid.

Results and discussion

The use of isotherms, separation factors, selectivity coefficients and the thermodynamic constants have proved helpful in describing equilibria in ion exchange systems. The interaction in the systems under investigation was described in terms of the equations

\[ \bar{C}_\text{Na} + C_{\text{Al}} \rightleftharpoons \bar{C}_\text{Al} + C_{\text{Na}} \]  \hspace{1cm} [1]

and

\[ \bar{C}_\text{Ca} + C_{\text{Al}} \rightleftharpoons \bar{C}_\text{Al} + C_{\text{Ca}} \]  \hspace{1cm} [2]

where bars represent the equivalent concentrations of the ion concerned in the clay (illite) phase and \( C_{\text{Na}} \), \( C_{\text{Ca}} \) and \( C_{\text{Al}} \), the electrolyte concentration of the ion concerned in the solution. The equivalent ionic fractions \( \tilde{X}_\text{Al} \), \( \tilde{X}_\text{Na} \), and \( \tilde{X}_\text{Ca} \) of the counter ions in illite and \( X_\text{Al} \), \( X_\text{Na} \) and \( X_\text{Ca} \) the corresponding equivalent
ionic fractions of these ions in solution were calculated from the expressions
\[ X_{Al} = \frac{\tilde{C}_{Al}}{C}, \quad X_{Na} = \frac{\tilde{C}_{Na}}{C} \]
\[ \tilde{C} = \tilde{C}_{Al} + \tilde{C}_{Na} \]
where \( \tilde{C} \) is the total electrolyte concentration in the clay phase and \( C \) that in the solution. The values obtained for the equivalent ionic fractions at 25 and 50 °C are given in tables 1–2. The exchange isotherms were plotted in figs. 1 and 2. At 25 °C there was preference of the clay for Ca over Al throughout the whole range. At 50 °C the isotherm was S shaped (11) indicating a strong preference of illite for Al at low values of \( X_{Al} \) and for Ca at high values. The isotherms of the Al—Na system both at 25 and 50 °C show that Na ions were strongly preferred by illite at all concentrations, the preference at 25 °C being somewhat greater than at 50 °C.

The affinity of illite for the interacting ions was further examined by the separation factors (tables 1–2)
\[ \alpha_{Ca}^{Al} = \left( \frac{X_{Al}}{X_{Ca}} \right) \left( \frac{X_{Ca}}{X_{Al}} \right) \]

and
\[ \alpha_{Na}^{Al} = \left( \frac{X_{Al}}{X_{Na}} \right) \left( \frac{X_{Na}}{X_{Al}} \right) \]

and by the quotients,
\[ K_{C} = \left( \frac{X_{Al}}{X_{Ca}} \right) \left( \frac{X_{Ca}}{X_{Na}} \right) \]

for the Al—Ca interaction

The values of \( K_{C} \) (tables 1–2) at different temperatures were

Table 1. Values of equivalent ionic fraction of aluminium, separation factor and selectivity quotient

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>25 °C</th>
<th>50 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_{Al} )</td>
<td>( X_{Ca} )</td>
<td>( X_{Ca} )</td>
</tr>
<tr>
<td>1.</td>
<td>0.165</td>
<td>0.588</td>
</tr>
<tr>
<td>2.</td>
<td>0.254</td>
<td>0.772</td>
</tr>
<tr>
<td>3.</td>
<td>0.343</td>
<td>0.893</td>
</tr>
<tr>
<td>4.</td>
<td>0.440</td>
<td>0.963</td>
</tr>
<tr>
<td>5.</td>
<td>0.501</td>
<td>0.983</td>
</tr>
<tr>
<td>6.</td>
<td>0.480</td>
<td>0.991</td>
</tr>
<tr>
<td>7.</td>
<td>0.545</td>
<td>0.995</td>
</tr>
<tr>
<td>8.</td>
<td>0.531</td>
<td>0.996</td>
</tr>
<tr>
<td>9.</td>
<td>0.576</td>
<td>0.998</td>
</tr>
<tr>
<td>10.</td>
<td>0.617</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Fig. 1. Exchange isotherm and separation factor for aluminium ion on calcium illite at different temperatures
plotted against $X_{Al}$ (figs. 3–4). $K_C$ increases with increasing values of $X_{Al}$ in all cases.

For a further study of the equilibria the thermodynamic equilibrium constant $K$ was calculated from the relationship

$$\ln K = \int \ln K_C dX_{Al}. \quad [7]$$

Table 2. Values of equivalent ionic fractions of aluminium, separation factor and selectivity quotient

<table>
<thead>
<tr>
<th>No.</th>
<th>25 °C</th>
<th>50 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.209</td>
<td>0.211</td>
</tr>
<tr>
<td>2.</td>
<td>0.284</td>
<td>0.288</td>
</tr>
<tr>
<td>3.</td>
<td>0.321</td>
<td>0.379</td>
</tr>
<tr>
<td>4.</td>
<td>0.326</td>
<td>1.257</td>
</tr>
<tr>
<td>5.</td>
<td>0.998</td>
<td>0.998</td>
</tr>
<tr>
<td>6.</td>
<td>0.372</td>
<td>0.983</td>
</tr>
<tr>
<td>7.</td>
<td>0.439</td>
<td>0.983</td>
</tr>
<tr>
<td>8.</td>
<td>0.479</td>
<td>0.988</td>
</tr>
<tr>
<td>9.</td>
<td>0.471</td>
<td>0.990</td>
</tr>
<tr>
<td>10.</td>
<td>0.520</td>
<td>0.991</td>
</tr>
</tbody>
</table>

The integrals were evaluated from the areas under the curves (figs. 3–4) using the trapezoidal rule (7). The values of the thermodynamic equilibrium constant $K$ were found to be higher at 50 °C (table 3) in both the systems indicating that the affinity of illite for Al increased with a rise in temperature. Also the values of $K$ in the
Table 3. Thermodynamic values of the exchanges Al—Ca and Al—Na on illite at 25 and 50 °C

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>Al—Ca system</th>
<th>Al—Na system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>50 °C</td>
</tr>
<tr>
<td>K</td>
<td>1204</td>
<td>1730</td>
</tr>
<tr>
<td>C° (Cal/mole)</td>
<td>+ 71408</td>
<td>+1111992</td>
</tr>
<tr>
<td>H° (Cal/mole)</td>
<td>-3943000</td>
<td>-398500</td>
</tr>
<tr>
<td>S° (Cal/mole)</td>
<td>15600</td>
<td>15600</td>
</tr>
</tbody>
</table>

The results indicate that exchange of Na- or Ca-ions by Al-ions is connected with a decrease in enthalpy. The negative enthalpy changes are presumably due to smaller ionic radii and higher charge of Al ions as compared to Ca and Na.

The negative $\Delta H^o$ is over compensated by the entropy term. The preference for Na and Ca could be due to entropy effects. The decrease in entropy accompanying the exchange of sodium and calcium ions by aluminium ions may be a consequence of the different double layer structures of sodium and aluminium ions. With sodium ions, the double layer structure is more extended and the distribution of cations above the negative illite surface is more diffuse than in the case of Al-ions, which may be arranged in a more ordered structure.

Fig. 4. Aluminium-sodium selectivity in illite

Al/Ca system were higher than in the Al/Na system indicating that the affinity of illite for Al was somewhat higher in the Al/Ca system.

The Gibbs free energies for the interactions [1] and [2] were obtained by eq. [8]

$$\Delta G^o = -RT\ln K.$$  \[8\]

Positive $\Delta G^o$ values (table 3) for the two interactions indicated that both at 25 and 50 °C, Na and Ca had a higher preference for illite than Al, which was in accordance with the assumptions drawn from the adsorption isotherms.

The standard enthalpy changes, $\Delta H^o$, were calculated from the Van't Hoff isochore

$$\ln \left( \frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right).$$  \[9\]

From $\Delta G^o$ and $\Delta H^o$ the standard free entropy changes were calculated in table 3.

Acknowledgment

The second author (Dr. R. P. Singh) is grateful to the C.S.I.R., New-Delhi for providing financial support.

Summary

A thermodynamic study has been made of the ion exchange of Na- and Ca-illite with Al ions. From the exchange isotherms at 25 and 50 °C the changes in free energy, enthalpy and entropy for the reactions were calculated. The isotherms, separation factors and free energy changes indicated a preference of Na and Ca ions by the illite.

References


Authors' address:
J. P. Singhal, R. P. Singh, and D. Kumar
Chemical Laboratories
Faculty of Engineering and Technology
Muslim University
Aligarh (India)
### Table 1 — Values of Equivalent Ionic Fractions and Selectivity Quotients at 30° and 60° for the Zn Exchange on Na-Illite

<table>
<thead>
<tr>
<th>$X_{Zn}$</th>
<th>$X_{Ca}$</th>
<th>$X_{Na}$</th>
<th>$X_{Na}$</th>
<th>$K_C$</th>
<th>$\log K_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.112</td>
<td>0.305</td>
<td>0.080</td>
<td>0.694</td>
<td>0.2246</td>
<td>0.6486</td>
</tr>
<tr>
<td>0.159</td>
<td>0.524</td>
<td>0.481</td>
<td>0.467</td>
<td>0.0969</td>
<td>1.0137</td>
</tr>
<tr>
<td>0.204</td>
<td>0.623</td>
<td>0.579</td>
<td>0.376</td>
<td>0.0728</td>
<td>1.0137</td>
</tr>
<tr>
<td>0.242</td>
<td>0.695</td>
<td>0.757</td>
<td>0.305</td>
<td>0.0565</td>
<td>1.2480</td>
</tr>
<tr>
<td>0.246</td>
<td>0.746</td>
<td>0.754</td>
<td>0.254</td>
<td>0.0371</td>
<td>1.4386</td>
</tr>
<tr>
<td>0.249</td>
<td>0.779</td>
<td>0.751</td>
<td>0.221</td>
<td>0.0277</td>
<td>1.5575</td>
</tr>
<tr>
<td>0.399</td>
<td>0.803</td>
<td>0.601</td>
<td>0.197</td>
<td>0.0536</td>
<td>1.2708</td>
</tr>
<tr>
<td>0.427</td>
<td>0.866</td>
<td>0.573</td>
<td>0.134</td>
<td>0.0270</td>
<td>1.5686</td>
</tr>
<tr>
<td>0.439</td>
<td>0.910</td>
<td>0.561</td>
<td>0.089</td>
<td>0.0122</td>
<td>1.9136</td>
</tr>
<tr>
<td>0.482</td>
<td>0.924</td>
<td>0.518</td>
<td>0.075</td>
<td>0.0116</td>
<td>1.9335</td>
</tr>
<tr>
<td>0.604</td>
<td>0.931</td>
<td>0.396</td>
<td>0.069</td>
<td>0.0206</td>
<td>1.6861</td>
</tr>
<tr>
<td>0.646</td>
<td>0.946</td>
<td>0.400</td>
<td>0.054</td>
<td>0.0118</td>
<td>1.9882</td>
</tr>
<tr>
<td>0.666</td>
<td>0.951</td>
<td>0.354</td>
<td>0.049</td>
<td>0.0108</td>
<td>1.9666</td>
</tr>
</tbody>
</table>

**EXPERIMENTS AT 30°**

<table>
<thead>
<tr>
<th>$X_{Zn}$</th>
<th>$X_{Ca}$</th>
<th>$X_{Na}$</th>
<th>$X_{Na}$</th>
<th>$K_C$</th>
<th>$\log K_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.066</td>
<td>0.324</td>
<td>0.593</td>
<td>0.676</td>
<td>0.1067</td>
<td>-0.9718</td>
</tr>
<tr>
<td>0.133</td>
<td>0.446</td>
<td>0.867</td>
<td>0.553</td>
<td>0.1213</td>
<td>-0.9162</td>
</tr>
<tr>
<td>0.133</td>
<td>0.573</td>
<td>0.867</td>
<td>0.426</td>
<td>0.0558</td>
<td>-1.2334</td>
</tr>
<tr>
<td>0.235</td>
<td>0.617</td>
<td>0.765</td>
<td>0.382</td>
<td>0.0850</td>
<td>-1.0223</td>
</tr>
<tr>
<td>0.319</td>
<td>0.646</td>
<td>0.680</td>
<td>0.354</td>
<td>0.1336</td>
<td>-0.8742</td>
</tr>
<tr>
<td>0.329</td>
<td>0.686</td>
<td>0.670</td>
<td>0.314</td>
<td>0.1046</td>
<td>-0.9805</td>
</tr>
<tr>
<td>0.402</td>
<td>0.738</td>
<td>0.593</td>
<td>0.134</td>
<td>0.0793</td>
<td>-1.8795</td>
</tr>
<tr>
<td>0.424</td>
<td>0.825</td>
<td>0.576</td>
<td>0.174</td>
<td>0.0464</td>
<td>-1.4335</td>
</tr>
<tr>
<td>0.458</td>
<td>0.893</td>
<td>0.542</td>
<td>0.170</td>
<td>0.0191</td>
<td>-1.7190</td>
</tr>
<tr>
<td>0.480</td>
<td>0.901</td>
<td>0.520</td>
<td>0.098</td>
<td>0.0197</td>
<td>-1.7055</td>
</tr>
<tr>
<td>0.528</td>
<td>0.911</td>
<td>0.471</td>
<td>0.088</td>
<td>0.0208</td>
<td>-1.4819</td>
</tr>
<tr>
<td>0.530</td>
<td>0.939</td>
<td>0.470</td>
<td>0.061</td>
<td>0.0102</td>
<td>-1.9914</td>
</tr>
<tr>
<td>0.590</td>
<td>0.945</td>
<td>0.410</td>
<td>0.055</td>
<td>0.0111</td>
<td>-1.9547</td>
</tr>
</tbody>
</table>

**EXPERIMENTS AT 60°**

<table>
<thead>
<tr>
<th>$X_{Zn}$</th>
<th>$X_{Ca}$</th>
<th>$X_{Na}$</th>
<th>$X_{Na}$</th>
<th>$K_C$</th>
<th>$\log K_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.076</td>
<td>0.468</td>
<td>0.924</td>
<td>0.532</td>
<td>0.0934</td>
<td>-1.0297</td>
</tr>
<tr>
<td>0.157</td>
<td>0.588</td>
<td>0.843</td>
<td>0.412</td>
<td>0.1304</td>
<td>-0.8848</td>
</tr>
<tr>
<td>0.211</td>
<td>0.620</td>
<td>0.749</td>
<td>0.380</td>
<td>0.2053</td>
<td>-0.6898</td>
</tr>
<tr>
<td>0.396</td>
<td>0.600</td>
<td>0.604</td>
<td>0.400</td>
<td>0.4370</td>
<td>-0.3595</td>
</tr>
<tr>
<td>0.474</td>
<td>0.692</td>
<td>0.526</td>
<td>0.307</td>
<td>0.3997</td>
<td>-0.3982</td>
</tr>
<tr>
<td>0.471</td>
<td>0.754</td>
<td>0.529</td>
<td>0.246</td>
<td>0.2904</td>
<td>-0.5374</td>
</tr>
<tr>
<td>0.609</td>
<td>0.797</td>
<td>0.390</td>
<td>0.203</td>
<td>0.3977</td>
<td>-0.4004</td>
</tr>
<tr>
<td>0.748</td>
<td>0.807</td>
<td>0.252</td>
<td>0.192</td>
<td>0.7062</td>
<td>-0.1311</td>
</tr>
<tr>
<td>0.819</td>
<td>0.828</td>
<td>0.181</td>
<td>0.171</td>
<td>0.9344</td>
<td>-0.0295</td>
</tr>
<tr>
<td>0.864</td>
<td>0.846</td>
<td>0.136</td>
<td>0.154</td>
<td>1.1564</td>
<td>-0.0630</td>
</tr>
</tbody>
</table>

### Table 2 — Values of Equivalent Ionic Fractions and Selectivity Quotients at 30° and 60° for the Zn Exchange on Ca-Illite

<table>
<thead>
<tr>
<th>$X_{Zn}$</th>
<th>$X_{Ca}$</th>
<th>$X_{Zn}$</th>
<th>$X_{Ca}$</th>
<th>$K_C$</th>
<th>$\log K_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.073</td>
<td>0.524</td>
<td>0.027</td>
<td>0.476</td>
<td>0.0715</td>
<td>-1.1457</td>
</tr>
<tr>
<td>0.191</td>
<td>0.595</td>
<td>0.029</td>
<td>0.405</td>
<td>0.1607</td>
<td>-0.7941</td>
</tr>
<tr>
<td>0.313</td>
<td>0.583</td>
<td>0.068</td>
<td>0.417</td>
<td>0.3263</td>
<td>-0.4864</td>
</tr>
<tr>
<td>0.422</td>
<td>0.576</td>
<td>0.278</td>
<td>0.424</td>
<td>0.5374</td>
<td>-0.2697</td>
</tr>
<tr>
<td>0.482</td>
<td>0.688</td>
<td>0.218</td>
<td>0.312</td>
<td>0.4219</td>
<td>-0.3748</td>
</tr>
<tr>
<td>0.554</td>
<td>0.735</td>
<td>0.246</td>
<td>0.4461</td>
<td>0.3560</td>
<td></td>
</tr>
<tr>
<td>0.628</td>
<td>0.807</td>
<td>0.372</td>
<td>0.193</td>
<td>0.4037</td>
<td>-0.3939</td>
</tr>
<tr>
<td>0.737</td>
<td>0.822</td>
<td>0.262</td>
<td>0.177</td>
<td>0.6057</td>
<td>-0.2177</td>
</tr>
<tr>
<td>0.784</td>
<td>0.847</td>
<td>0.215</td>
<td>0.153</td>
<td>0.6886</td>
<td>-0.1814</td>
</tr>
<tr>
<td>0.820</td>
<td>0.789</td>
<td>0.180</td>
<td>0.121</td>
<td>0.6968</td>
<td>-0.1569</td>
</tr>
</tbody>
</table>

**EXPERIMENTS AT 30°**

**EXPERIMENTS AT 60°**

---

**Fig. 1 — Plots of equivalent ionic fractions of zinc in illites against that in solution**
observed in the case of Na-illite. From the isotherms it was also inferred that the illite clay had a higher preference for Na ions as compared with Ca ions at 30°. However, the effect at 60° was variable.

To examine the interaction in the liquid and illite phases the selectivity coefficients at 30° and 60° for different surface compositions of Zn were determined from the expressions\(^8,10\) (3 and 4) taking the ratio of activity coefficients as unity\(^9\) in the dilute range studied.

\[
K_C = \frac{\frac{X_{Zn}}{X_{Na}}}{\frac{X_{Na}}{X_{Zn}}} \text{ for the Na-Zn exchange} \quad \ldots (3)
\]

\[
K_C = \frac{X_{Zn} \times X_{Ca}}{X_{Ca} \times X_{Zn}} \text{ for the Ca-Zn exchange} \quad \ldots (4)
\]

The values for \(K_C\) (Tables 1 and 2) at different temperatures were plotted against \(X_{Zn}\) (Fig. 2). An examination of the plots revealed that while the selectivity coefficients during the Ca-Zn exchange increased with an increase in the value of \(X_{Zn}\) there was a continuous decrease with a small rise in between, in the values of selectivity coefficients during Na-Zn exchange. The pattern of behaviour was the same at both the temperatures in the two cases. Such a variation was in accordance with the preference shown by Zn for the Ca-clay as compared to Na-illite (Fig. 1).

For a further study of the affinity the thermodynamic equilibrium constants \(K\) were calculated from the relationship proposed by Gaines and Thomas\(^9\).

\[
\ln K = (Z_a - Z_b) + \int_0^1 \ln K_C \, dX_{Zn} \quad \ldots (5)
\]

where \(Z_a\) and \(Z_b\) represent the charges on the competing ions. The integrals were evaluated from the areas under the curves (Fig. 2) using the trapezoidal rule\(^11\). Some uncertainty was involved in this evaluation. The isotherms were extrapolated at both the ends. Although justification\(^13,14\) for the extrapolation was available from an examination of the linearity and finite slope of the isotherms at large and small values of \(X_{Zn}\), the values of \(K\) obtained could not be classed as exact. In the discussion that follows, the values for the equilibrium constant and other thermodynamic parameters given in Table 3 have, therefore, been considered qualitatively only.

The values of the thermodynamic equilibrium constant (Table 2) were found to be lower at 30°.

![Fig. 2 — Plots of selectivity quotient (log \(K_C\)) against equivalent ionic fractions of zinc in illites](image-url)
Table 3 — Thermodynamic Parameters for the Zn Exchange on Na- and Ca-Illite at 30° and 60°

<table>
<thead>
<tr>
<th>Thermodynamic parameter</th>
<th>Na-Zn system</th>
<th>Ca-Zn system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°</td>
<td>60°</td>
</tr>
<tr>
<td>$K$</td>
<td>0.0498</td>
<td>0.0672</td>
</tr>
<tr>
<td>$\Delta G^°$ (cal/mole)</td>
<td>+1820.85</td>
<td>+1775.95</td>
</tr>
<tr>
<td>$\Delta H^°$ (cal/mole)</td>
<td>+2275.61</td>
<td></td>
</tr>
<tr>
<td>$\Delta S^°$ (cal/mole/deg)</td>
<td>1.50</td>
<td></td>
</tr>
</tbody>
</table>

than at 60° in the Na-Zn system and higher at 30° than at 60° in the Ca-Zn system. These were indicative of the fact that the affinity of Na-illite for zinc increased with a rise in temperature while that of Ca-illite decreased. Also the higher values of $K$ in the Ca-Zn system as compared to the Na-Zn system indicated that the affinity of Ca-illite for Zn was somewhat greater than that of Na-illite for Zn.

The positive $\Delta G^°$ values ($\Delta G^° = -RT \ln K$) (Table 3) for the interactions indicated that both at 30° and 60°, Na and Ca had a higher preference for illite than Zn and their replacement from illite by Zn could not be spontaneous.

The standard enthalpy changes $\Delta H^°$ were calculated from the Van't Hoff isochore (6)

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

The values are given in Table 3. It may be mentioned that the values of enthalpy calculated above were not the enthalpies of exchange alone. They included the enthalpies of hydration, dilution, mixing and exchange. Also the method of determination by measuring equilibrium constants at two different temperatures involved an approximation to the extent of ±1 to 2 kcal, although where a small temperature range was involved Eq. 6, gave reasonably satisfactory values.

A positive enthalpy effect during the Na-Zn exchange pointed to a stronger binding of Na as compared to Zn on the illite surface. A small negative enthalpy change during Ca-Zn exchange, however, pointed to a somewhat stronger binding of Zn as compared to Ca on the illite surface, which appeared to be contrary to the assumptions drawn from the adsorption isotherms.

The standard entropy changes $\Delta S^°$ were calculated by the equation $\Delta G^° = \Delta H^° - T \Delta S^°$ and the values are given in Table 3. The observation based on enthalpy found support from the entropy changes during the exchanges. The entropy changes arose from the randomness and disorder in the exchanger and solution phases as well as the hydration and dehydation of ions taking part in the exchange. Although a positive entropy effect during the Na-Zn exchange may be in agreement with a higher preference on Na ions on the illite surface, yet it indicated a diffused and disordered arrangement of Zn ions in the Gouy layer and a more ordered arrangement of Na ions in the Stern layer. The greater disorder in the system appeared to be due to the depletion of the hydration shell around Zn ions caused by Na ions during the exchange reactions. On the other hand a negative entropy effect during the Ca-Zn exchange indicated that the hydration shell around Zn ions remained intact with Zn being bound at fixed, specific sites on the illite surface producing a greater order in the system.

Valence, electrostatic considerations, the ion sizes and the nature of the diffused electrical double layer in the two exchanges justified these assumptions.

Acknowledgement

One of the authors (D.K.) is grateful to the UGC, New Delhi, for providing a junior fellowship.

References

Thermodynamics of Ion Exchange Equilibria Involving Fe" Superscript + Ion on Na"—Montmorillonite

J. P. SINGHAL, R. P. SINGH and DINESH KUMAR

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

Manuscript received 2 April 1974; revised 5 November 1974; accepted 1 March 1975

An attempt has been made to study the mechanism of Fe"+—Na" exchange on montmorillonite

FeCl₃ solution with the help of isotherm studies. From the exchange isotherms at 25° and 60° the

reaction coefficients were calculated; these were compared with those obtained from thermodynamic

studies. The ion exchange was also found to be dependent on the concentration of Na" ions for the clay phase. The results were used to evaluate the true concentration of Fe"+ and Na" and then to determine the deviation of the clay system from ideality.

Experimental

The clay used was montmorillonite from Amori, Mathura. It was dispersed in distilled water and

suspended in 2 N NaCl—montmorillonite mixtures containing 2 N NaCl. A small quantity of

60.1% HCl was kept in an hour and the supernatant solution discarded. This treatment was repeated

during times and the solutions removed from the Montmorillonite suspension by washing with
distilled water and alcohol until the clay dispersed and the conductivity of the aqueous suspension was of

the same order as that of distilled water (10⁻⁴ mhos/cm). It was then quickly used for the cation-exchange

experiments to avoid any ageing effects. The concentration of the suspension was 5.40 g/litre.

For the determination of the exchange isotherms the clay suspension was washed with very dilute

NaCl solution. This also eliminated the possibility of hydroxide precipitation. 20.0 ml each of sodium montmorillonite

clay suspension was taken in several stoppered test tubes and varying volumes of 0.02 N ferric sulfate solution added and the mixture adjusted to a constant volume with distilled water. The tubes were shaken for three hours at 25° ± 0.1° in the first set of experiments and 60° ± 0.1° in the second set of experiments in a thermostatically regulated bath. The mixtures were then centrifugated and the Na" and Fe"+ in the supernatant liquid estimated. Na" was

measured flame photometrically, and Fe"+ colorimetrically with Beuch and Lomb spectronic-20 at 540 nm using orthophenanthroline as colour reagent. The pH values of these equilibrium solutions were found to vary between 3.0 to 3.3. The CEC of montmorillonite was measured by the ammonium-acetate method of Jackson. The corresponding concentrations for Na" in clay phase were obtained by difference (CEC-concentration of the cation in the supernatant liquid) and that for Fe"+ from Fe"+ added minus the cation in the supernatant liquid.

Results and Discussion

The interaction between the Fe"+ ions in solution and the Na" ions on the clay surface may be represented by the equation:

\[ C_{Na^+} + C_{Fe^+} = C_{Fe^+} + C_{Na^+} \]  \( \text{(1)} \)

The barred quantities refer to the equivalent concentrations of the ion concerned in the clay phase and \( C_{Na^+} \) and \( C_{Fe^+} \) the electrolyte concentration in the solution. The equivalent ionic fractions of Fe"+ and Na" in montmorillonite and in the solution were calculated from the expressions:

\[ X_{Na^+} = \frac{C_{Na^+}}{C} \]

\[ X_{Fe^+} = \frac{C_{Fe^+}}{C} \]

\[ \frac{C_{Na^+}}{C} = X_{Na^+} \]

\[ \frac{C_{Fe^+}}{C} = X_{Fe^+} \]

\[ X_{Na^+} + X_{Fe^+} = 1 \]  \( \text{(2)} \)
where \( \bar{C} \) and \( C \) were the total electrolyte concentrations in the clay and solution phases respectively. The values obtained both at 30° and 60° are given in Table 1. The data yielded the exchange isotherms vide Fig. 1. The isotherms were of the Langmuir type, showed a strong preference by montmorillonite for \( \text{Na}^+ \) as against \( \text{Fe}^{3+} \) with no selectivity reversal and depended on temperature; the affinity for \( \text{Fe}^{3+} \) increasing with a rise in temperature.

To examine the interaction in the liquid and clay phases represented by equation (1) and taking the ratio of the activity coefficients in the liquid phase in the range of concentration studied by us as unity, the selectivity coefficients at various values of \( X_{Fe} \) were calculated from the expression

\[
K_e = \frac{(\bar{X}_{Fe})(\bar{X}_{Na})^3}{(\bar{X}_{Na})^3 (\bar{X}_{Fe})} \quad ... (3)
\]

A plot of the values of \( K_e \) obtained at different temperatures (Table 1) for \( \text{Na}^+ - \text{Fe}^{3+} \) exchange in 0.54% montmorillonite suspensions is given in Fig. 2. The selectivity coefficient, on an average, showed a decrease with increasing concentration of \( \text{Fe}^{3+} \) on montmorillonite. The variation in the selectivity coefficient with composition of the surface phase \( (\bar{X}_{Fe}) \) indicated that there were significant interactions between the neighbouring ions on the surface of montmorillonite due to differences in the electrostatic attraction or binding energy of the exchange sites arising from tetrahedral vs octahedral substitution.

For a further study of the affinity the thermodynamic equilibrium constant \( K \) was calculated by the equation

\[
\ln K = (Z_A - Z_B) + \int \ln K_d \bar{X}_{Fe^{3+}} \quad ... (4)
\]

where \( Z_A \) and \( Z_B \) were the valences of the competing ions. The integral was evaluated from the area under the curves (Fig. 2) using the trapezoidal rule. The value of \( K \) at 30° was lower than at 60° (Table 2) indicating that the affinity of \( \text{Fe}^{3+} \) for montmorillonite increased with a rise in temperature, a result in accordance with the deductions drawn from the nature of adsorption isotherms.

The Gibbs free energy change for the exchange reaction was calculated using the relation

\[
\Delta G^\circ = -RT \ln K \quad ... (5)
\]

The standard enthalpy change \( \Delta H^\circ \) was calculated from the Vant Hoff isochore

\[
\ln \left( \frac{K_{T_2}}{K_{T_1}} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad ... (6)
\]

and the standard entropy change by the equation

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad ... (7)
\]

The thermodynamic values obtained are summarized in Table 2. The values were qualitative and could not be calculated with the desired accuracy.
The reaction was attended by positive enthalpy effects i.e., the adsorption increased with a rise in temperature, a fact in accordance with our observations. The increase in enthalpy calculated\(^1\) that, Fe\(^{3+}\) was less strongly bound with the clay than Na\(^+\) and the exchange of Na\(^+\) with Fe\(^{3+}\) may not be easy in the above system.

The exchange was also ruled by entropy effects. The preference for Na\(^+\) could be due to entropy effects. The decrease in entropy accompanying the exchange of Na\(^+\) by Fe\(^{3+}\) ions could be a consequence of the different double layer\(^1\) structures of Na\(^+\) and Fe\(^{3+}\) ions. With Na\(^+\) ions the double layer was more extended and the distribution of cations above the negative montmorillonite surface was more diffuse than in the case of Fe\(^{3+}\) ions which might be arranged in a more ordered structure.

The activity coefficients of the cations at the surface were calculated from the following relations\(^4\)

\[
\ln f_{Na} = \ln f_{Fe} + \ln f_{Fe^{3+}} \quad \text{in } E_{Na^{+}}-\text{E}_{Fe^{3+}^{+}}\quad (8)
\]

\[
\text{and} \quad \ln f_{Fe} = \ln f_{Na} - f_{Fe^{3+}} \quad \text{in } E_{Fe^{3+}}-\text{E}_{Na^{+}}\quad (9)
\]

The values obtained are given in Table 3. Large values were obtained for the surface phase activity coefficients of Fe\(^{3+}\) at the clay-surface ions at 30° and 60°. High values for activity coefficients in solid phase have been reported by other workers\(^7\) also in case of ions with unlike changes interacting on non-ideal surfaces. Such values of activity coefficients, therefore, were indicative of a marked heterogeneity at the clay surface with significant interactions between the Na\(^+\) and Fe\(^{3+}\) ions at the neighbouring sites of the surface.

because of the uncertainty about the energy of hydration of adsorbed ions. At a rate of fast \(\Delta H\) values included the enthalpies of hydration, dilution, mixing, and exchange.

Table 2—Thermodynamic values for Fe\(^{3+}\) exchange with sodium montmorillonite at 30° and 60°

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>(E_{Fe}^{3+})</th>
<th>(E_{Fe}^{3+})</th>
<th>(E_{Fe}^{3+})</th>
<th>(E_{Fe}^{3+})</th>
<th>log(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.125</td>
<td>0.320</td>
<td>0.747</td>
<td>0.970</td>
<td>-1.143</td>
</tr>
<tr>
<td>2.</td>
<td>0.177</td>
<td>0.716</td>
<td>0.213</td>
<td>0.970</td>
<td>-2.835</td>
</tr>
<tr>
<td>3.</td>
<td>0.205</td>
<td>0.590</td>
<td>0.127</td>
<td>0.970</td>
<td>-3.232</td>
</tr>
<tr>
<td>4.</td>
<td>0.215</td>
<td>0.613</td>
<td>0.702</td>
<td>0.968</td>
<td>-3.523</td>
</tr>
<tr>
<td>5.</td>
<td>0.215</td>
<td>0.603</td>
<td>0.663</td>
<td>0.968</td>
<td>-3.796</td>
</tr>
<tr>
<td>6.</td>
<td>0.205</td>
<td>0.565</td>
<td>0.543</td>
<td>0.968</td>
<td>-3.061</td>
</tr>
<tr>
<td>7.</td>
<td>0.205</td>
<td>0.523</td>
<td>0.597</td>
<td>0.964</td>
<td>-3.387</td>
</tr>
<tr>
<td>8.</td>
<td>0.231</td>
<td>0.605</td>
<td>0.051</td>
<td>0.964</td>
<td>-3.338</td>
</tr>
<tr>
<td>9.</td>
<td>0.221</td>
<td>0.605</td>
<td>0.041</td>
<td>0.964</td>
<td>-3.387</td>
</tr>
<tr>
<td>10.</td>
<td>0.221</td>
<td>0.623</td>
<td>0.023</td>
<td>0.965</td>
<td>-3.387</td>
</tr>
<tr>
<td>11.</td>
<td>0.251</td>
<td>0.742</td>
<td>0.023</td>
<td>0.965</td>
<td>-3.796</td>
</tr>
<tr>
<td>12.</td>
<td>0.256</td>
<td>0.757</td>
<td>0.022</td>
<td>0.965</td>
<td>-3.796</td>
</tr>
</tbody>
</table>

The activity coefficients of the cations at the surface were calculated from the following relations\(^4\)

\[
\ln f_{Na} = \ln f_{Fe} + \ln f_{Fe^{3+}} \quad \text{in } E_{Na^{+}}-\text{E}_{Fe^{3+}^{+}}\quad (8)
\]

\[
\text{and} \quad \ln f_{Fe} = \ln f_{Na} - f_{Fe^{3+}} \quad \text{in } E_{Fe^{3+}}-\text{E}_{Na^{+}}\quad (9)
\]

Table 3—The surface phase activity coefficients for different Na\(^+\)-Fe\(^{3+}\) compositions at the clay surface at 30° and 60°

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>(E_{Fe}^{3+})</th>
<th>(f_{Na})</th>
<th>(f_{Fe}^{3+})</th>
<th>(f_{Fe}^{3+})</th>
<th>(f_{Fe}^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.123</td>
<td>0.320</td>
<td>0.747</td>
<td>0.970</td>
<td>-1.143</td>
</tr>
<tr>
<td>2.</td>
<td>0.177</td>
<td>0.716</td>
<td>0.213</td>
<td>0.970</td>
<td>-2.835</td>
</tr>
<tr>
<td>3.</td>
<td>0.205</td>
<td>0.590</td>
<td>0.127</td>
<td>0.970</td>
<td>-3.232</td>
</tr>
<tr>
<td>4.</td>
<td>0.215</td>
<td>0.613</td>
<td>0.702</td>
<td>0.968</td>
<td>-3.523</td>
</tr>
<tr>
<td>5.</td>
<td>0.215</td>
<td>0.603</td>
<td>0.663</td>
<td>0.968</td>
<td>-3.796</td>
</tr>
<tr>
<td>6.</td>
<td>0.205</td>
<td>0.565</td>
<td>0.543</td>
<td>0.968</td>
<td>-3.061</td>
</tr>
<tr>
<td>7.</td>
<td>0.205</td>
<td>0.523</td>
<td>0.597</td>
<td>0.964</td>
<td>-3.387</td>
</tr>
<tr>
<td>8.</td>
<td>0.231</td>
<td>0.605</td>
<td>0.051</td>
<td>0.964</td>
<td>-3.338</td>
</tr>
<tr>
<td>9.</td>
<td>0.221</td>
<td>0.605</td>
<td>0.041</td>
<td>0.964</td>
<td>-3.387</td>
</tr>
<tr>
<td>10.</td>
<td>0.221</td>
<td>0.623</td>
<td>0.023</td>
<td>0.965</td>
<td>-3.387</td>
</tr>
<tr>
<td>11.</td>
<td>0.251</td>
<td>0.742</td>
<td>0.023</td>
<td>0.965</td>
<td>-3.796</td>
</tr>
<tr>
<td>12.</td>
<td>0.256</td>
<td>0.757</td>
<td>0.022</td>
<td>0.965</td>
<td>-3.796</td>
</tr>
</tbody>
</table>

Positive \(\Delta G^0\) values both at 30° and 60° indicated that Fe\(^{3+}\) had a smaller preference for the montmorillonite surface than Na\(^+\) in accordance with the earlier assumptions.

The excess thermodynamic functions play an important part in expressing the deviation of a heterogeneous system from ideality. The excess thermodynamic functions for the formation of a heterogeneous
Na\textsuperscript+–Fe\textsuperscript{3+} exchanger were calculated from the activity coefficients. Thus, the excess free energy of mixing \( \Delta G_m^e \) was calculated from the relationship\textsuperscript{13}

\[
\Delta G_m^e = RT(\bar{x}_{Fe} \ln f_{Fe} + \bar{x}_{Na} \ln f_{Na})
\]

... (10)

The excess enthalpy of mixing was calculated using the expression\textsuperscript{4}

\[
\Delta H_m^e = -RT \left[ \bar{x}_{Fe} \left( \frac{\partial \ln f_{Fe}}{\partial T} \right) + \bar{x}_{Na} \left( \frac{\partial \ln f_{Na}}{\partial T} \right) \right]
\]

... (11)

The excess entropy of mixing was then calculated by the equation

\[
\Delta G_m^e = \Delta H_m^e - T \Delta S_m^e
\]

... (12)

The values are tabulated in Table 4.

The excess free energy of mixing plotted against equivalent ionic fraction in the clay is given in Fig. 3. It was positive and increased with concentration of the Fe\textsuperscript{3+} ion at both temperatures. This is indicative\textsuperscript{14} of the fact that the heterogeneous mixture of Na\textsuperscript+ and Fe\textsuperscript{3+} phases on the clay surface was less stable as compared to the pure hemihydrate forms i.e., the deviation from ideality occurred in the sense of a less stable mixture. This presumably was due to a variation in the hydration state of the randomly interstratified Na\textsuperscript+ rich and Fe\textsuperscript{3+} rich layers on the montmorillonite surface.

The \( \Delta G_m^e \) is also ruled by enthalpy and entropy effects. The excess entropy change of mixing \( \Delta S_m^e \) was generally negative (Table 4) at both the

<table>
<thead>
<tr>
<th>Sl.</th>
<th>( \bar{x}_{Fe} )</th>
<th>( \Delta G_m^e )</th>
<th>( \Delta H_m^e )</th>
<th>( \Delta S_m^e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.126</td>
<td>65.54</td>
<td>-383.67</td>
<td>-1.48</td>
</tr>
<tr>
<td>2.</td>
<td>0.177</td>
<td>187.14</td>
<td>-749.07</td>
<td>-9.02</td>
</tr>
<tr>
<td>3.</td>
<td>0.205</td>
<td>302.96</td>
<td>-833.15</td>
<td>-5.54</td>
</tr>
<tr>
<td>4.</td>
<td>0.210</td>
<td>392.57</td>
<td>-1032.12</td>
<td>-4.40</td>
</tr>
<tr>
<td>5.</td>
<td>0.231</td>
<td>337.18</td>
<td>-1205.82</td>
<td>-5.09</td>
</tr>
<tr>
<td>6.</td>
<td>0.239</td>
<td>377.88</td>
<td>-1205.82</td>
<td>-5.23</td>
</tr>
<tr>
<td>7.</td>
<td>0.254</td>
<td>448.37</td>
<td>-1607.76</td>
<td>-6.78</td>
</tr>
</tbody>
</table>

... (10)

\[
\Delta G_m^e = \Delta H_m^e - T \Delta S_m^e
\]

Fig. 2. Logarithms of selectivity quotient vs Equivalent ionic fraction of iron in montmorillonite.
temperatures. $\Delta S_\text{sys}$ could be a measure of the nature of distribution of the Na$^+$ and Fe$^{3+}$ ions on the montmorillonite surface as compared to the pure forms. Its negative values for our mixed system pointed to a more ordered distribution of the mixture of Fe$^{3+}$ and Na$^+$ ion on the clay surface as compared to the pure forms at all concentrations under study.

Acknowledgement

The second author is indebted to C.S.I.R. for the grant of a fellowship.

References

Aluminium-Nicotine Exchange Equilibria on Illite (Part II)

J. P. SINGHAL, K. P. SINGH and D. KUMAR
Engineering Chemistry Laboratory, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh

Aluminium-nicotine exchange equilibria in dilute suspensions of illite were studied at 25° and 40°. Exchange isotherms were drawn and thermodynamic equilibrium constants and the standard free energies of exchange were evaluated from the selectivity coefficients. The results indicated a preference of nicotine by the clay system at both the temperatures up to a limited concentration. The negative enthalpy effects and entropy loss accompanying the reaction showed a stronger and more ordered binding of the nicotinium ions on the clay surface. Values of surface phase activity coefficients of the adsorbed ions and the excess thermodynamic functions indicated that the equilibria involving aluminium and nicotine behaved as a non-ideal system.

ILLITE occurs widely as a constituent of illitic soils. Its ion exchange properties have been of considerable interest both for theoretical and practical reasons. The toxicity and acidity of aluminium in soils is of considerable interest. Clays show a strong preference for aluminium ion in dilute solutions and it is almost impossible to exchange it with other ions. Such, however, is not the case with concentrated solutions.

Nicotine is a base and a pesticide. It plays an important role in the functions of the central nervous system. Studies in these laboratories and elsewhere revealed that acidic illites interact stoichiometrically with nicotine and other heterocyclic bases. The interaction was a base exchange one, in which, the adsorption of nicotine occurred up to the base exchange capacity.

In the study of ion exchange it has been recognised that although the two ions may exchange stoichiometrically, they would not, in general, be held equally strongly by the exchanger. Preference by the exchanger plays an important role in ion exchange reactions. Thus, it became desirable to study in detail the ion exchange reactions into which aluminium and nicotine participate in terms of the thermodynamic functions and surface phase activity coefficients. The basis of the treatment have been the thermodynamic formulations of previous workers. It has been felt that such a study will throw considerable light on the mechanism of nicotine adsorption and release on aluminium illites.

Experimental

The clay mineral illite used in these studies was from Morris, Illinois and was a monomineralic standard of the clay mineral standards Project No. 49 of the American Petroleum Institute. The less than two micron clay fraction was isolated by sedimentation and centrifugation at a speed of 3000 rpm by filtering through the bowl of the "International Chemical" centrifuge. The clay suspension was equilibrated with 2 N NaCl and 0.1 N HCl for half an hour. The supernatant salt solution was decanted. This treatment was repeated three times and chloride ions removed from the sodium clay suspension by washing with distilled water till the clay dispersed and till the filtrate was free of chloride ions.

To obtain aluminium illite the sodium illite suspension was treated with normal aluminium chloride solution. The suspension was then washed with distilled water till the resistance of the suspension became of the same order as that of distilled water. The concentration of the suspension was 1.28 g/100 ml and its pH = 4.0.

Nicotine was purified by distilling at 98° and 4 mm pressure in an inert atmosphere.

For the determination of exchange isotherms, 10.0 ml each of aluminium illite suspension was taken in different stoppered glass tubes. Various concentrations of standard nicotine solution (0.5 g per 100 ml) were immediately added and the mixture adjusted to 25 ml with distilled water. The tubes were shaken at 25°±0.1° in the first set of experiments and 40°±0.1° in the second set of experiments for 24 hr in a thermostatic bath. The mixtures were then centrifuged immediately and aluminium and nicotine in the supernatant liquid estimated. The aluminium was estimated colorimetrically using aluminon as colour reagent and nicotine with standard hydrochloric acid using methyl red as indicator. The CEC of illite was measured by the ammonium acetate method of Jackson. The corresponding concentrations of aluminium in the clay phase were obtained by difference (CEC minus concentration of cation in the supernatant liquid) and that for nicotine from nicotine added minus the nicotine in the supernatant liquid.
Results and Discussion

The interaction in the aluminium-nicotine system in dilute suspensions can be described by the equation

\[ \hat{C}_{\text{Al}} + C_{\text{nicotine}} \rightleftharpoons C_{\text{Al}} + \hat{C}_{\text{nicotine}} \]  \hspace{1cm} (1)

where bars represent the equivalent concentration of the ion concerned in the solid phase and unbarred quantities the electrolyte concentration in solution.

The equivalent ionic fractions of aluminium and nicotine in illite and in the solution were calculated from the expressions

\[ \bar{X}_{\text{Al}} = \frac{C_{\text{Al}}}{C}, \quad X_{\text{Al}} = \frac{C_{\text{Al}}}{C}, \quad \bar{X}_{\text{nicotine}} = \frac{C_{\text{nicotine}}}{C}, \quad X_{\text{nicotine}} = \frac{C_{\text{nicotine}}}{C} \]

and \( X_{\text{nicotine}} = \frac{C_{\text{nicotine}}}{C} \), where \( C \) was the total electrolyte concentration in the clay phase and \( C \) that in the solution (\( C = C_{\text{Al}} + C_{\text{nicotine}} \) and \( C = C_{\text{Al}} + C_{\text{nicotine}} \)). The values obtained both at 25° and 40° are given in Table 1. A plot of these values gave exchange isotherms as in Fig. 1. At both the temperatures the isotherms were sigmoid and showed selectivity reversal. Nicotine was strongly preferred by the clay up to an equivalent ionic fraction of 0.64 of nicotine at 25° and up to 0.62 of nicotine at 40°. Thereafter the aluminium preference for illite showed an upward trend.

To examine the interaction in the clay phase, the selectivity coefficients at 25° and 40° for different surface compositions of nicotine were determined from the expression\(^{11}\), (assuming the ratio of activity coefficients as unity\(^2\) in the dilute range studied):

\[ K_C = \frac{(X_{\text{nicotine}})^n}{(X_{\text{Al}})^n} \]  \hspace{1cm} (2)

The values are summarised in Table 1 and the effect of nicotine concentration on these values represented as in Fig. 2. At both the temperatures the selectivity quotient after an initial rise decreased and then rose again. Such a behaviour, in general, was indicative of the fact that at both the temperatures beyond
a certain concentration, the preference of the solid surface for nicotine decreased with a rise in its concentration and thereafter rose again. It thus appeared that there were significant interactions between the nicotine and the multiple sites of aluminium illite which underwent gradual saturation one after another.

For a further study of the affinity the thermodynamic equilibrium constant K was calculated by the equation proposed by Gaines and Thomas:

$$\ln K = (Z_A - Z_B) + \int_0^1 \ln K_N d\overline{X}_{nicotine}$$

(3)

where $Z_A$ and $Z_B$ were the charges of the competing ions. Evaluating the integral with the help of trapezoidal rule and substituting the other values, the values of K at 25° and 40° were calculated. The value of K at 25° was higher than that at 40° indicating that nicotine had a higher affinity for the aluminium clay at 25° than at 40°. The interaction was temperature dependent.

The standard free energy of exchange $\Delta G^\circ$ for the interaction was calculated using the relation

$$\Delta G^\circ = -RT \ln K$$

(4)

The standard enthalpy change $\Delta H^\circ$ was calculated from the Vant' Hoff isochore

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

(5)

and the standard entropy change by the equation

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

(6)

The values obtained are given in Table 2.

### Table 2—Thermodynamic Values for the Nicotine Exchange with Aluminium Illite at 25° and 40°

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>25°</th>
<th>40°</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>25.79</td>
<td>14.88</td>
</tr>
<tr>
<td>$\Delta G^\circ$ Cal/mole</td>
<td>-1927.02</td>
<td>-1668.79</td>
</tr>
<tr>
<td>$\Delta H^\circ$ Cal/mole</td>
<td>-7057.09</td>
<td>-167.09</td>
</tr>
<tr>
<td>$\Delta S^\circ$ Cal/mole</td>
<td>-17.21</td>
<td>-17.21</td>
</tr>
</tbody>
</table>

The negative values of $\Delta G^\circ$ both at 25° and 40° indicated that the illite surface had a higher preference for nicotine than aluminium; that at 25° being still higher than at 40°.

Negative enthalpy effects showed that the adsorption of nicotine decreased with rise in temperature. The decrease in enthalpy indicated that nicotine was more strongly bound to the clay surface than aluminium and the exchange of nicotine with aluminium may not be easy in the concentration range studied.

The adsorption of nicotine was accompanied by entropy loss. The decrease in entropy indicated a reversible system with nicotinium ions forming a very well placed ordered arrangement in the Stern layer and aluminium ions forming a diffused arrangement in the Gouy layer. This fact was in accordance with the preference shown by the illite surface for nicotine.

The surface activity coefficients of aluminium and nicotinium ions at the surface were calculated from the following expressions:

$$\ln f_{A1} = \overline{X}_{nicotine} \ln K_C - \int_0^1 \ln K_N d \overline{X}_{nicotine}$$

(7)

and

$$\ln f_{nicotine} = (\overline{X}_{nicotine} - 1) \ln K_C - \int_0^1 \ln K_N d \overline{X}_{nicotine}$$

(8)

The values are given in Table 3 and were plotted against mole fraction ($\overline{X}_{nicotine}$) (Figs. 3-4).
absence of similarity in the plots of the surface phase activity coefficients $f_{\text{n}}$ and $f_{\text{nicotine}}$ against ionic fraction of nicotine indicated that both nicotine and aluminium behaved differently on the illite surface (Table 3). At both the temperatures, up to an equivalent ionic fraction of 0.52 of nicotine the values of surface phase activity coefficient of aluminium were greater than unity while those of nicotine were throughout less than unity. Significantly beyond this equivalent ionic fraction these values became less than unity in case of aluminium also.

The deviation of the activity coefficients from unity indicated a heterogeneous distribution of the ions at the clay surface. Thus, it seemed that the distribution and the freedom of movement of the two ions in the Gouy and Stern layers varied according to the concentration of nicotine added to Al-illite. The results found support from the work of Deist and Talibudeen on ion exchange in soils.

### Table 3—Activity Coefficient of the Adsorbed Ions as a Function of Nicotine Fraction in Illite at 25° and 40°

<table>
<thead>
<tr>
<th>$X_{\text{nicotine}}$</th>
<th>$f_{\text{nicotine}}$</th>
<th>$f_{\text{Al}}$</th>
<th>$X_{\text{nicotine}}$</th>
<th>$f_{\text{nicotine}}$</th>
<th>$f_{\text{Al}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.211</td>
<td>1.271</td>
<td>0.126</td>
<td>0.290</td>
<td>1.127</td>
<td>0.346</td>
</tr>
<tr>
<td>0.352</td>
<td>1.391</td>
<td>0.097</td>
<td>0.353</td>
<td>1.522</td>
<td>0.164</td>
</tr>
<tr>
<td>0.521</td>
<td>1.221</td>
<td>0.113</td>
<td>0.520</td>
<td>1.234</td>
<td>0.204</td>
</tr>
<tr>
<td>0.663</td>
<td>0.167</td>
<td>0.127</td>
<td>0.655</td>
<td>0.173</td>
<td>0.136</td>
</tr>
<tr>
<td>0.792</td>
<td>0.098</td>
<td>0.133</td>
<td>0.766</td>
<td>0.093</td>
<td>0.057</td>
</tr>
<tr>
<td>0.804</td>
<td>0.060</td>
<td>0.368</td>
<td>0.775</td>
<td>0.071</td>
<td>0.705</td>
</tr>
<tr>
<td>0.815</td>
<td>0.045</td>
<td>0.372</td>
<td>0.812</td>
<td>0.110</td>
<td>0.638</td>
</tr>
<tr>
<td>0.826</td>
<td>0.045</td>
<td>0.383</td>
<td>0.860</td>
<td>0.198</td>
<td>0.563</td>
</tr>
<tr>
<td>0.847</td>
<td>0.050</td>
<td>0.375</td>
<td>0.887</td>
<td>0.216</td>
<td>0.560</td>
</tr>
<tr>
<td>0.864</td>
<td>0.055</td>
<td>0.372</td>
<td>0.900</td>
<td>0.206</td>
<td>0.560</td>
</tr>
</tbody>
</table>

The values of surface activity coefficients (Table 3) indicated that the system under investigation did not behave ideally. The excess thermodynamic functions for such a non-ideal system were calculated by the equations:

\[
\Delta G_m^e = RT \ln \left( X_{\text{nicotine}} X_{\text{Al}} - 1 \right) \]  \quad (9)
\[
\Delta H_m^e = -RT \left( \ln X_{\text{nicotine}} + \frac{\partial \ln f_{\text{nicotine}}}{\partial T} X_{\text{Al}} \right) \]  \quad (10)
\[
\Delta S_m^e = -T \left( \frac{\partial \ln f_{\text{nicotine}}}{\partial T} X_{\text{Al}} \right) \]  \quad (11)

where $\Delta G_m^e$, $\Delta H_m^e$ and $\Delta S_m^e$ were the excess free energy, enthalpy and entropy of mixing. The values are given in Table 4. A plot of the excess free energy of mixing against $X_{\text{nicotine}}$ is given in Fig. 5. At both the temperatures the excess free energies of mixing were negative, the value first increased and thereafter decreased with increasing concentration of $X_{\text{nicotine}}$. It thus appeared that the heterogeneous mixture of aluminium and nicotine ions on the illite surface was initially more stable as compared to the pure homionic forms and thereafter became less or more stable depending upon the concentration of nicotine. Thus, deviation from ideality occurred in the form of a more or less stable mixture depending upon the equivalent ionic fraction of nicotine.

Negative enthalpies and entropies of mixing (Table 4) indicated that the ions were strongly bound with each other at the clay surface and the
distribution of the mixture of aluminium and nicotinium ions was more ordered an the heteroionic exchange with respect to the pure homoionic forms.

Acknowledgement

The second author is indebted to C.S.I.R. for the grant of a senior fellowship.

References
