Abstract—The form under which ethylenediamine (EDA) is adsorbed from aqueous solution by hydrogen- and ethylenediammonium-montmorillonite was studied as a function of the amount of amine present in the system.

EDA added to the acid clay in quantities lower than or equal to the cation exchange capacity (C.E.C.) was exclusively adsorbed as ethylenediammonium (EDAH$_3^+$) ion. On further addition of amine the pH of the suspension rose to alkaline values and the monoprotonated species (EDAH$^+$) was the main charge balancing cation.

Evaporating at room temperature "EDA-H-montmorillonite-H$_2$O" or "EDA-EDAH$_3^+$-montmorillonite-H$_2$O" systems containing 300 me EDA/100 g clay did not cause loss of nitrogen, but degassing under high vacuum (10$^{-6}$ mm Hg) did. Nevertheless, excess EDA molecules with respect to the C.E.C. were retained on the clay surface, at the expense of water molecules, through strong asymmetrical hydrogen bonds between their NH$_2$ groups and the NH$_3^+$ groups of EDAH$^+$ ions. On heating up to 160$^\circ$C under vacuum the nitrogen content decreased further, but still remained at a level significantly higher than the C.E.C. value, all NH$_3^+$ groups remaining involved in strong hydrogen bonding. It is suggested that a "condensation" process takes place, implying evolution of EDA molecules and giving rise to "polymeric" associations between protonated and unprotonated diamine.

Washing the clay suspensions with distilled water did not completely remove excess EDA either, as a consequence of the equilibrium existing between the ionic species in solution (EDAH$_3^+$ and EDAH$^+$) and on the clay surface. It seems that these species were preferentially adsorbed as "trimeric" associations in which two out of four NH$_3^+$ groups are hydrogen bonded to NH$_2$ groups. After heating at 200$^\circ$C, nitrogen retained on the clay surface was mainly in the form of NH$_4^+$ ions. Ammonium formation was enhanced by the presence of excess EDA and was considerably faster than in montmorillonite systems containing EDA coordinated to Cu$^{2+}$ ions.

INTRODUCTION

The nature of the exchangeable cation is one of the most important factors determining the adsorption mechanism of alkylamines by clay surfaces and hence the kind and stability of the amino-clay complexes formed. As shown in part I of this study (Laura and Cloos, 1970), with Cu$^{2+}$ ion, a definite and stable coordination complex is obtained, whether ethylene-diamine is added as pure liquid to an air-dry montmorillonite film, or as aqueous solution to a montmorillonite suspension.

On acid clay, protonation of the adsorbed amine is the expected mechanism. This has actually been observed by Fripiat et al. (1962), Servais et al. (1962) for propyl- and butyl-amine, ethylene- and propylene-diamine, and by Mortland and Barák (1964) for ethylamine. The same authors report that ethylamine, ethylene- and propylene-diamine are adsorbed in amounts largely exceeding the cation exchange capacity of the clay. Similarly, ethylamine is adsorbed by ethylenammonium montmorillonite (Farmer and Mortland, 1965). This is interpreted in terms of competition between water and amine molecules to associate with the alkylammonium cations through hydrogen bonding. It must, however, be pointed out that the above mentioned studies were performed on non-aqueous systems. Servais et al. (1962) treated freeze-dried
montmorillonite with a benzene solution of amine, whereas Mortland et al. (1964, 1965) exposed a vacuum evacuated clay film to ethylamine vapor.

A priori, it may be assumed that in aqueous medium the amine is not necessarily as successful a competitor as in dehydrated systems. The fact that ethylamine is displaced from the ethylamine-ethylammonium complex by water vapor at room humidity (Farmer and Mortland, 1965) sufficiently justifies this assumption. On the other hand, from the work of Servais et al. (1962) and Fripiat et al. (1962) it appears that monoamines and diamines do not behave in the same manner. In contrast with what is observed for ethylene- and propylene-diamine, propyl- and butyl-amine-montmorillonite systems show no excess retention with respect to the C.E.C. after washing with an essentially non polar solvent such as benzene.

Therefore, it seemed of interest to the authors, to carry out this adsorption study on aqueous suspension, and to compare the thermal stability of the compounds obtained in these conditions with that of the copper-ethylenediamine complex investigated previously (Laura and Clots, 1970).

MATERIALS AND METHODS

The clay used was montmorillonite from Camp-Berteau (Morocco). Its cation exchange capacity (C.E.C.), measured with NH₄⁺ ion at pH 7, amounts to 103 ± 3 me/100 g. H-montmorillonite was prepared by passing a 1 per cent suspension of Na-montmorillonite (< 2 µ fraction) through a column of hydrogen saturated Amberlite IR-120 resin. This suspension was used immediately after preparation in order to keep the level of conversion of H- to Al-clay as low as possible (Eeckman and Laudelout, 1961). EDAH₂-montmorillonite was obtained by treating the < 2 µ Na-clay fraction three times with an excess of 1.0N solution of ethylenediamine dihydrochloride, and then washing it with distilled water on the centrifuge until free of chloride.

The experimental methods used were the same as described in part I (Laura and Cloos, 1970). Different amounts of EDA were added to 50 ml portions of 1% clay suspensions (Fig. 1), and after equilibration overnight, the samples were investigated before and after washing three times with distilled water. X-ray and i.r. spectra were recorded on thin oriented clay films (3-4 mg/cm²). Nitrogen was determined by micro-Kjeldahl technique.

RESULTS

Potentiometric titration curves

The potentiometric titration curves of different clay suspensions with EDA solution are compared in Fig. 1. With H-montmorillonite, like Cu-
of amine added was adsorbed on the clay and resisted removal by washing. On further addition a supplementary quantity was retained against washing. Similarly, EDAH₂ montmorillonite adsorbs EDA which cannot be removed completely by washing, the adsorption level considerably exceeding the C.E.C. value.

**X-ray data**

The basal spacings \(d(001)\) of the different systems studied are compared in Table 2. They show the effect of four factors: (1) amount of amine adsorbed, (2) outgassing at room temperature, (3) heating under vacuum, and (4) nature of the saturating cation. They increased slightly as the degree of adsorption went beyond the C.E.C. value. Outgassing at ambient temperature caused a small decrease in spacing; the experimental values obtained compare fairly well with those reported by Léonard et al. (1962). Heating under vacuum reduced the basal spacing and provoked interstratification. This phenomenon started at 80°C for sample 1, partially saturated with EDA, and at 120°C for the other samples. Complete structure collapse at 200°C was observed only for the reference and washed EDAH₂ montmorillonite samples. After rehydration reexpansion to the original value did not take place in any case. The spacings of H-montmorillonite were generally 0.3-0.4 Å higher than those of EDAH₂ montmorillonite for equivalent EDA contents.

**I.R. data**

Provided samples with comparable N contents are considered, the i.r. spectra are broadly similar, whether the starting material was H- or EDAH₂ montmorillonite. This is illustrated in Fig. 2 showing spectra of the different systems after outgassing at ambient temperature. In the case of acid clay, bands are generally less distinct, probably as a consequence of a lower degree of homogeneity due to partial aluminization of the starting material. Spectra recorded on samples containing different levels of EDA showed significant differences.
mainly in the position and shape of the N–H bands. Table 3 gives the band assignments as suggested by data in the literature (Powell, 1960; Sabatini and Califano, 1960; J. Bellanato, 1960; Fripiat et al., 1962) and will be discussed later.

The stretching region of each spectrum is dominated by a broad absorption extending from 3350 to 2200 cm\(^{-1}\) with a main band near 3200 cm\(^{-1}\). As the N content increased beyond the C.E.C. value, this band sharpens, becomes more symmetric and its maximum shifts to higher frequencies. Simultaneously a new band of low intensity develops near 3360 cm\(^{-1}\) which is assigned to \(\nu\)NH\(_2\) asym. of excess unprotonated or monoprotonated EDA. In the 2800–1700 cm\(^{-1}\) range, absorption is slightly enhanced, two diffuse, weak and broad bands emerging near 2500–2400 cm\(^{-1}\) and 2000 cm\(^{-1}\) respectively. The 1843 cm\(^{-1}\) band is probably due to the clay structure as it is already present in pure montmorillonite. C–H vibrations in the 2800–3000 cm\(^{-1}\) region appear more or less distinct. In the deformation region the two prominent bands near 1500 and 1600 cm\(^{-1}\) correspond to the \(\delta\)NH\(_3^+\) sym. and \(\delta\)NH\(_3^+\) asym. vibration modes respectively, while the weaker absorptions in the 1450–1470 cm\(^{-1}\) range are due to CH\(_2\) scissoring. Excess adsorption of EDA affected the position of the high frequency band little, but resulted in broadening, especially for samples containing more than 200 me N/100 g (curves e and f). Moreover, in this latter case two maxima may be distinguished near 1637 and 1600 cm\(^{-1}\) and seem to be related to contributions from \(\delta\)NH\(_3^+\) asym. and \(\delta\)NH\(_2\) sci. vibrations. Band broadening and development of two diffuse maxima, near 1538 and 1510 cm\(^{-1}\) respectively, are also shown by the \(\delta\)NH\(_3^+\) sym. absorption when EDA is retained against washing in excess of the C.E.C. (curves c and d). This might be interpreted as an indication of the existence of two different environments for the NH\(_3^+\) groups on the clay surface. When EDA adsorption exceeds 200 per cent of the C.E.C. (curves e and f) one single \(\delta\)NH\(_3^+\) sym. band of medium intensity remains near 1540 cm\(^{-1}\). These results differ from those of Fripiat et al. (1962) who observed no \(\delta\)NH\(_3^+\) sym. band in the 1500 cm\(^{-1}\) region on samples containing more than 50 mmoles of EDA, but only one absorption at 1597 cm\(^{-1}\) which they assigned to \(\delta\)NH\(_2\) sci. vibration.
Table 3. Vibration bands and their assignment for EDA adsorbed on H- and EDAH₂-montmorillonite

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>Normal frequencies in cm⁻¹</th>
<th>Deuterated frequencies in cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>vOH (hyd. water)</td>
<td>3400</td>
<td>2597</td>
</tr>
<tr>
<td>vNH₂ asym.</td>
<td>3362</td>
<td>2516</td>
</tr>
<tr>
<td>vNH₄⁺</td>
<td>3280</td>
<td>-</td>
</tr>
<tr>
<td>vNH₂ sym. (+ vNH₃⁺)</td>
<td>3226</td>
<td>2424</td>
</tr>
<tr>
<td>vCH₂ asym.</td>
<td>2963</td>
<td>2963</td>
</tr>
<tr>
<td>vCH₂ sym.</td>
<td>2899</td>
<td>2890</td>
</tr>
<tr>
<td>vN–H...N</td>
<td>2439 (b)</td>
<td>1835 (b)</td>
</tr>
<tr>
<td>δOH (hyd. water)</td>
<td>1634</td>
<td>-</td>
</tr>
<tr>
<td>δN–H...N asym.</td>
<td>1637</td>
<td>-</td>
</tr>
<tr>
<td>δNH₃⁺ asym.</td>
<td>1617</td>
<td>-</td>
</tr>
<tr>
<td>δNH₂ sci.</td>
<td>1600</td>
<td>-</td>
</tr>
<tr>
<td>δN–H...N sym.</td>
<td>1538</td>
<td>-</td>
</tr>
<tr>
<td>δN–H...OH₂ sym.</td>
<td>1530</td>
<td>-</td>
</tr>
<tr>
<td>δNH₄⁺ sym.</td>
<td>1510</td>
<td>-</td>
</tr>
<tr>
<td>δCH₂ sci.</td>
<td>1465</td>
<td>1460</td>
</tr>
<tr>
<td>δNH₄⁺</td>
<td>1449</td>
<td>1447</td>
</tr>
</tbody>
</table>

ν—Stretching; δ—Deformation; asym.—asymmetric; sym.—symmetric; sci.—scissoring; (b)—broad.

This discrepancy might arise from the fact that these authors prepared oriented films by pressing powdered clay between stainless steel disks, which probably did not assure the same degree of orientation as slow evaporation of dilute clay suspensions.

The data obtained in this work are more nearly comparable to the findings of Farmer and Mortland (1965) on the ethylamine-ethylammonium system. After adsorption of ethylamine on ethylammonium montmorillonite they observed the replacement of the δNH₃⁺ sym. (1510 cm⁻¹) and δNH₄⁺ asym. (1617 cm⁻¹) absorptions respectively, by a diffuse shoulder extending from 1580 to 1510 cm⁻¹ and by two bands at 1642 and 1593 cm⁻¹. In their opinion the 1593 cm⁻¹ vibration is due to NH₂ scissoring, whereas the high frequency band can be ascribed to the proton involved in symmetric hydrogen bonding between the components of a dimer of structure

\[
\begin{align*}
\text{Et} & \quad \begin{array}{c}
\text{H}
\end{array} \\
\text{H} & \quad \begin{array}{c}
\text{N} \ldots \text{H} \quad \text{N} \quad \text{H}
\end{array} \\
\text{H} & \quad \begin{array}{c}
\text{Et}
\end{array}
\end{align*}
\]

The effect of degassing and heating under vacuum is illustrated in Fig. 3. The changes brought about in the i.r. spectra by this treatment are the same for EDAH₂– and EDA–H–montmorillonite. Air-dried samples (curves a, f and k) show strong absorptions by hydration water near 3400 and 1634 cm⁻¹, which obscure the N–H bands of the respective regions. On dehydration the δNH₃⁺ sym. band shifts progressively from 1530 to 1508 cm⁻¹ in the case of samples containing no excess EDA (Figs. 3A, b and 2, a and b). When a large excess of EDA was present (Fig. 3C, 1), the shift occurs in the opposite direction (1538 cm⁻¹) accompanied by a decrease of the absorption intensity. A similar weakening of the δNH₃⁺ sym. absorption was recorded for samples containing a moderate excess of EDA (Fig. 3B, g).

Heating to 120°C did not cause major modifications of the spectra, except a further decrease of the δNH₃⁺ sym. bands of samples having retained excess EDA against washing (Fig. 3B, h). At 200°C a drastic change occurs in the spectra of all the samples: the N–H bands of NH₃⁺ and NH₂ groups are replaced by strong, sharp NH₄⁺ absorptions at 1429 and 3280 cm⁻¹. Simultaneously, three rather weak bands appear at 1667, 1608 and 1303 cm⁻¹ which might be associated with decay products of EDA (Laura and Cloos, 1970). In samples containing excess EDA, ammonium ion formation commenced at 160°C (Figs. 3B, i and 3C, n). It should also be noted that at 200°C C–H vibrations in the 2800–3000 cm⁻¹ region and near 1465 cm⁻¹ persist; their intensities seem to be proportional to those of the three bands attributed to decay products, which in turn depend on the N contents of the respective samples.

DISCUSSION

The inflection point of the titration curve of H–montmorillonite (Fig. 1) corresponds to an amount of EDA equalling the C.E.C. value (Table 1, sample 2). This indicates that EDA was adsorbed as divalent EDAH₂⁺ ion up to complete saturation of the C.E.C. Further support for this conclusion is provided by the similarity of the i.r. spectra of pure EDAH₂–montmorillonite and of H–montmorillonite treated with EDA (Fig. 2, a and b). The findings of Fripiat et al. (1962) were similar, whereas Conley and Lloyd (1971) suggested that on the surface of H–kaolinite EDA functions as a monoamine, one single NH₂ group being protonated. The adsorption mechanism involved is obviously proton transfer from the clay surface to EDA, according to

\[
2 \text{mont.–H} + \text{EDA} \rightarrow (\text{mont.–})_2 \text{EDA}H_2
\]

As proposed by Servais et al. (1962), Al³⁺ ions present in acid clay may participate in amine
adsorption through the following dissociation:

$\text{(mont.-)}_3 \text{Al(H}_2\text{O)}_6 \rightleftharpoons 3 \text{mont.-H} + \text{Al(OH)}_3 + 3\text{H}_2\text{O}$

The formation of Al(OH)$_3$ in the interlamellar space might account for the slight discrepancies in the basal spacings (Table 2) observed between EDAH$_2$- and H-montmorillonite with comparable N contents.

Upon addition of EDA in excess of the C.E.C., the pH of the suspension rose as a consequence of the following equilibria:

$\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_3^+ + \text{OH}^- \quad (1)$

$\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{N}^+\text{-CH}_2\text{-CH}_2\text{-NH}_3^+ + \text{OH}^- \quad (2)$

with

$K_{B_1} = \frac{[\text{EDA}\text{H}^+][\text{OH}^-]}{[\text{EDA}]} = 5.15 \times 10^{-4} \text{ at } 0{\circ}\text{C}$

and

$K_{B_2} = \frac{[\text{EDA}\text{H}_2^{2+}][\text{OH}^-]}{[\text{EDA}\text{H}^+]} = 3.66 \times 10^{-7} \text{ at } 0{\circ}\text{C}$

(Weast, 1969)

Hence, the clay particles were in the presence of three different species, i.e. EDA, EDAH$^+$ and EDAH$_2^{2+}$, the relative concentrations of which vary with pH (Table 4) and influence the composition of the adsorbate. At equilibrium the suspensions of samples 3unw and 4unw gave a pH of approximately 10, at which EDAH$^+$ was the predominant species in solution. Though the selectivity of charged clay surfaces is usually higher for divalent than for monovalent cations, and their acidity higher than that indicated by the pH of the

<table>
<thead>
<tr>
<th>pH</th>
<th align="right">[EDAH$_2^{2+}$] : [EDA] : [EDA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td align="right">$3.66 \times 10^4$ : 1 : 1.95 x 10$^{-8}$</td>
</tr>
<tr>
<td>4</td>
<td align="right">10$^3$ : 1 : 10$^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td align="right">10$^2$ : 1 : 10$^{-5}$</td>
</tr>
<tr>
<td>6</td>
<td align="right">10$^1$ : 1 : 10$^{-3}$</td>
</tr>
<tr>
<td>7</td>
<td align="right">1 : 1 : 1</td>
</tr>
<tr>
<td>8</td>
<td align="right">10$^{-1}$ : 1 : 10$^{-2}$</td>
</tr>
<tr>
<td>9</td>
<td align="right">10$^{-2}$ : 1 : 10$^{-2}$</td>
</tr>
<tr>
<td>10</td>
<td align="right">10$^{-3}$ : 1 : 10$^{-1}$</td>
</tr>
<tr>
<td>11</td>
<td align="right">10$^{-4}$ : 1 : 1</td>
</tr>
</tbody>
</table>

Table 4. Relative concentrations of EDA, EDAH$^+$ and EDAH$_2^{2+}$ species in aqueous solution at 0°C as a function of pH
ADSORPTION OF EDA ON MONTMORILLONITE 265

suspension, it may be assumed that EDAH\(^+\) was the main charge balancing cation. Since on removal of the equilibrium solution by centrifugation the quantity of diamine retained (expressed in me N/100 g) amounted to twice the C.E.C. (Fig. 4,b), suggests this conclusion. Washing again modified the composition of the adsorbate. The successive equilibrations with portions of distilled water caused release of EDAH\(^+\) ions from the clay surface into the liquid phase. But for each such ion lost, another EDAH\(^+\) ion, remaining on the clay, had to be converted into EDAH\(_2\)\(^+\) ion in order to satisfy charge compensation. The protons necessary for this conversion were produced by the dissociation of water, the hydroxyls insuring the electrical neutrality of the liquid phase. This process was very slow, as illustrated in Fig. 4,b, and explains why after three washings the montmorillonite suspension still had a pH of 9 and a N content exceeding the C.E.C. by roughly 50%.

In an aqueous system, therefore, retention of excess EDA against washing must not be interpreted (as in dry systems) in terms of competition between amine and water molecules for hydrogen bonding with polar NH\(_3\)\(^+\) groups.

Evaporation of the suspensions of the washed samples 3 and 4 probably did not significantly modify the status of the adsorbed species. The structural arrangement most compatible with the data of chemical analysis and equilibrium considerations in relation to pH and charge balancing requirements would be the following:

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{N} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{N} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{N} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

This arrangement is also consistent with the appearance of two symmetric NH\(_3\)\(^+\) deformation vibrations, at 1508 and 1538 cm\(^{-1}\) respectively (Figs. 2c, d and 3B, g). The former might be related to the terminal NH\(_3\)\(^+\) groups of the trimer, having the same environment as in pure EDAH\(_2\)-montmorillonite. The latter might correspond to the NH\(_3\)\(^+\) groups of the EDAH\(_2\)\(^+\) ion, hydrogen bonded with the NH\(_2\) groups of the adjacent EDAH\(^+\) ions. The shift to higher frequencies (from 1530 to 1538 cm\(^{-1}\)) with respect to hydrated samples suggests that hydrogen bonds between NH\(_3\)\(^+\) and NH\(_2\) were stronger than between NH\(_3\)\(^+\) and H\(_2\)O. This seems quite reasonable, as EDAH\(^+\) is a stronger base than water.

As shown in Table 1, excess retention of EDA against washing is less important on H-montmorillonite (sample 3) than on EDAH\(_2\)-montmorillonite (sample 4). This difference may be accounted for by a higher proportion of EDAH\(_2\)\(^+\) ions reflecting a higher surface acidity due to the presence of Al\(^3+\) ions in H-montmorillonite.

It is possible that the charge distribution in the trimer may be modified in the following manner

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

in order to insure a better geometric "fit" with a particular local charge distribution on the clay surface. As measured on scale models, the nitrogen atoms in trans EDA are separated by about 4 Å, and according to Pimentel and McClellan (1960) the average length of a N-H...N hydrogen bond

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**Fig. 4.** Effect of washing and of degassing under vacuum at increasing temperatures on the nitrogen content of different systems. EDAH\(_2\)-montmorillonite equilibrated with 0.017 N solution of EDA\(_2\)HCl (a), with 0.017 N solution of EDA (sample 4) (b); 0 washing = equilibrium solution removed. EDA-EDA\(_2\)-montmorillonite (sample 4 unw), air-dry ▲, degassed △(c).
is 3.1 Å. Thus, the extreme positive centers in the trimeric arrangement would be 18.2 Å distant. On the other hand, assuming a homogeneous charge distribution on the montmorillonite surface, it can be calculated that the mean distance between two negative sites is approximately 12 Å. By an appropriate translation of the adjacent sheets, one with respect to the other (which in an aqueous suspension is easily achievable), a different homogeneous distribution of negative sites in the interlamellar space, i.e. one every 6 Å alternatively on the upper and on the lower plate, can be realized. This configuration should be energetically advantageous, as repulsion between negative charges is reduced to a minimum. It is interesting to note that according to this assumption four negative sites can be distributed over a distance of 18 Å. Such a good fit with the trimeric arrangement might be a stabilizing factor for this form in the interlamellar space. The observed basal spacings (Table 2) are consistent with a monolayer of adsorbed species, the carbon chain being oriented parallelly to the silicate sheets (Léonard et al., 1962). In this position only one N–H of each NH₂⁺ group is able to hydrogen bond with an adjacent NH₂ group. The other two are in contact with the clay surface and may interact with surface oxygens. On this basis a trimer of the following configuration seems to be excluded.

\[
\text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_2 \quad \ldots \quad \text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_2
\]

On evaporation of the unwashed clay suspensions (samples 3 and 4) at ambient temperature no EDA is desorbed (Fig. 4,c). Since water was removed during this process, equilibria (1) and (2) in the liquid phase should continuously shift to the left until the film was air-dry. Degassing at room temperature caused only partial desorption of amine, and in the temperature range 120–160°C the nitrogen content in the EDA–EDA⁺–montmorillonite system still amounted to 2.25 times the C.E.C. value (Fig. 4,c). Therefore, it must be concluded that up to 160°C neutral EDA molecules were firmly retained on the clay surface, and competed on a favourable basis with water molecules for interaction with protonated amine groups and surface hydroxyls. The lower volatility of EDA with respect to water and the presence of two polar groups are probably the major reasons for this behaviour. The absence of the δNH₃ sym. band at 1508 cm⁻¹ and the presence of the 1538 cm⁻¹ absorption (Figs. 2,e,f and 3C,1,m) suggest that all NH₃⁺ groups are hydrogen bonded to NH₂ groups. From nitrogen determinations (Fig. 4,c) it can be inferred that in air-dry films one N atom out of three carried a positive charge. These requirements are satisfied by a trimer of the following structure

\[
\text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_2 \quad \ldots \quad \text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_2
\]

as suggested by Farmer and Mortland (1965). For samples outgassed at room temperature the N⁺:N⁺ + N ratio is 1:2.5 and increased to 1:2.25 after heating at 120°–160°C. Though during this treatment EDA molecules were desorbed, all NH₃⁺ groups remained hydrogen bonded to NH₂ groups as evidenced by i.r. spectroscopy (Fig. 3C,m,n). This observation may be accounted for by the following mechanism involving “condensation” of adjacent EDAH⁺...EDA associations with evolution of EDA molecules:

\[
4 \text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2 \quad \ldots \quad \text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_2 \\
\text{degassing at room temperature} \\
2\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2 \quad \ldots \quad \text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_2 \\
\text{heating at 120°–160°C} \\
\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2 \quad \ldots \quad \text{H}_3\text{N}-(\text{CH}_2)_2-\text{NH}_2
\]

It is conceivable that, as a consequence of the condensation process, a redistribution of the positive charges occurs in the “polymeric” associations in order to fit best the distribution pattern of negative charges on the clay surface. This can be realized by movement of a proton from one or the other NH₃⁺ group of an EDAH⁺ ion to a NH₂ group of a neighbouring EDA molecule or EDAH⁺ ion, giving rise to structures of types V and VI.

\[
[H_2\text{N}-(\text{CH}_2)_2-\text{NH}_3]_n \quad H_2\text{N}-(\text{CH}_2)_2-\text{NH}_2 \\
\quad \ldots \quad H_3\text{N}-(\text{CH}_2)_2-\text{NH}_2
\]

(V)

\[
[H_2\text{N}-(\text{CH}_2)_2-\text{NH}_3]_n \quad H_2\text{N}-(\text{CH}_2)_2-\text{NH}_2 \\
\quad \ldots \quad H_3\text{N}-(\text{CH}_2)_2-\text{NH}_2
\]

(VI)
where $n$ and $m$ vary with the amount of EDA molecules present and may be equal to 0, 1, 2, ... 

A particular feature of the infrared spectra of unwashed samples 3 and 4 is the broadening of the deformation band in the 1600 cm$^{-1}$ region with the appearance of two maxima near 1600 and 1637 cm$^{-1}$ (Figs. 2,e,f and 3C,k,l,m,n). The absorption at 1637 cm$^{-1}$ is very strong in the air-dry sample, and on degassing at ambient temperature, decreases much more than the one located at 1600 cm$^{-1}$. A similar behaviour is shown by the 3362 cm$^{-1}$ band, assigned to $\nu\text{NH}_2$ asym., with respect to the absorption at 3226 cm$^{-1}$. At first sight one is tempted to relate this decrease in intensity to the loss of EDA molecules. But its extent is in no way proportional to the fraction of EDA lost, and the respective bands are hardly affected by further desorption of EDA during heating the clay film. Therefore, it seems reasonable to assume that the main contribution to the 3362 and 1637 cm$^{-1}$ bands in the air-dry sample is due to adsorbed water. On the other hand, since adsorption of EDA in amounts largely exceeding the C.E.C. caused a shift of the $\delta\text{NH}_3^+$ sym. vibration to higher frequencies, a similar effect on the $\delta\text{NH}_3^+$ asym. band would be predicted. Hence, the 1637 and 1600 cm$^{-1}$ absorptions are assigned to $\delta\text{NH}_3^+$ asym. and $\delta\text{NH}_3$ sciss. vibrations respectively.

A shift of the deformation bands towards higher frequencies, as a consequence of hydrogen bonding, is generally accompanied by a shift towards lower frequencies of the corresponding stretching vibrations. Therefore, it would be expected that the prominent band at 3175 cm$^{-1}$ in pure EDAH$_2$-montmorillonite would shift to lower frequencies after adsorption of excess EDA; however the reverse is observed. Simultaneously two broad, diffuse bands develop near 2500-2400 and 2000 cm$^{-1}$ (Fig. 2,e,f), which might be related to $\bar{\text{N}}$-$\text{H}$...$\text{N}$ hydrogen bonding. Sample 4w also shows these bands (Fig. 2,c). In their infrared studies on hydrogen bonds in some adducts of phenols with their phenoxides and other oxygen bases, Hadži et al. (1963) attributed two broad but discrete maxima near 2500-2600 and 1800-1900 cm$^{-1}$ to stretching vibrations of OH involved in strong asymmetrical intermolecular hydrogen bonds. They also observed that the $\delta$-OH frequency increased but slightly. This pattern of absorption matches fairly well the one discussed here. The 3226 cm$^{-1}$ band (Fig. 2,e,f) is probably due to contributions of $\bar{\text{N}}$-H groups not involved in $\bar{\text{N}}$-$\text{H}$...$\text{N}$ associations (as only one out of three is able to participate in such hydrogen bonds), and to $\nu\text{N}^-$-$\text{H}$ sym. vibrations of NH$_2$ groups.

Assuming that isotopic exchange will proceed faster on NH$_3^+$ groups than on NH$_2$ groups, we deuterated samples containing increasing levels of EDA to different extents, in order to check the correctness of our band assignments. For this purpose clay films were degassed and exposed for 1 hr at room temperature to the vapour phase of H$_2$O-D$_2$O mixtures of varying H$_2$O/D$_2$O ratios. The samples were again degassed and their i.r. spectra were recorded. In these experiments the clay films used were thicker than usual (10-13 mg/cm$^2$ instead of 3-4 mg/cm$^2$), which resulted in higher absorption intensities, and the recording rate adopted was slower (0.04 $\mu$/min instead of 0.25 $\mu$/min), which caused an overall shift of the bands to slightly lower frequencies. Figure 5 compares the spectra of pure EDAH$_2$-montmorillonite and EDA-EDAH$_2$-montmorillonite containing an excess of 200 me EDA/100 g with respect to the C.E.C. (sample 4 unw) after 50% and 90% deuteration respectively. In case of unwashed sample 4 (curve b) the high frequency
band in the 1640–1590 cm⁻¹ region, assigned to \(\delta NH_2^+\) asym., disappears almost completely at 50% deuteration, while the low frequency band, ascribed to \(\delta NH_2\) sci., is much less affected. Likewise, the \(\delta NH_3^+\) sym. absorption near 1540 cm⁻¹ is no longer visible. In pure EDAH₂–montmorillonite (curve a), where deuteration could effect only half of the \(NH_3^+\) groups, the corresponding bands at 1605 and 1510 cm⁻¹ are still present. Thus, it seems that the 1637 cm⁻¹ band is due to \(\delta NH_3^+\) asym. vibration. In both samples the 1600 cm⁻¹ absorption might contain a contribution from \(NH_2D^+\) groups, and it is possible that the new band, appearing after deuteration in the 1420–1433 cm⁻¹ range, is due to \(\nu N–H\) vibration of the \(NHD^+\) group, as suggested by Powell (1960), and perhaps of the NHD group in case of sample 4unw. At 90% deuteration (curves c and d) the 1600 cm⁻¹ band has disappeared, whilst the 1420–1433 cm⁻¹ absorptions are still well pronounced, but less intense. On the basis of the proposed assignment a decrease in intensity would actually be expected as deuteration becomes nearly complete. In the 3400–3000 cm⁻¹ region the \(\nu N–H\) vibrations persist up to 90% deuteration. They decrease progressively with increasing degree of deuteration and the corresponding \(\nu N–D\) bands in the 2400–2000 cm⁻¹ range become stronger and stronger. A band near 2700 cm⁻¹ is obviously related to physically adsorbed D₂O. Its lower intensity in EDA–EDAHO–montmorillonite (curves b and d) confirms the observation of Servais et al. (1962), that water is largely replaced by EDA molecules on the clay surface.

Another interesting feature concerns the absorption intensity near 1835 cm⁻¹. Pure clay shows a broad band in this region, but in sample 4 (curves b and d) its intensity is considerably higher than in reference EDAH₂–montmorillonite (curves a and c), though the clay films were of equal thickness. The only reasonable explanation for the enhancement of intensity in this region is that it is due to \(\nu N–D\) vibrations of N–D...N associations, the hydrogen analogs of which absorb near 2440 cm⁻¹ (Fig. 2,e). The 1980 cm⁻¹ band is undistinguishable; it might be hidden by the broad inflexion in this region, or it might be shifted, on deuteration, to lower frequencies and overlapped by the strong \(\delta CH_2\) sci. absorptions near 1460–1447 cm⁻¹. All the samples show a band at 1914 cm⁻¹ which is probably due to the clay structure, but which cannot be distinguished on spectra taken with thinner films.

Whether or not the amount of EDA adsorbed exceeds the C.E.C. value, heating at 200°C under vacuum generated \(NH_4^+\) ions as indicated by the 3280 and 1429 cm⁻¹ bands (Fig. 3, e, j and o). In EDA–Cu–montmorillonite complexes, \(NH_4^+\) formation was also observed in the same experimental conditions, but to a much lower extent (Laura and Cloos, 1970). This indicates the EDA is considerably more stable on a montmorillonite surface when it is coordinated to Cu²⁺ ion, than when it is present in diprotonated, monoprotonated or neutral form. The fact that \(NH_4^+\) formation has already started at 160°C in samples containing excess amine is not explained (Fig. 3,i and n). It might be due to a higher degree of dissociation of residual water, present in smaller amounts in these samples (Mortland and Raman, 1968).

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REFERENCES
ADSORPTION OF EDA ON MONTMORILLONITE


Résumé—La forme sous laquelle l’éthylènediamine (EDA) est adsorbée à partir d’une solution aqueuse par la montmorillonite saturée en protons et en ions éthylènediammonium est étudiée en fonction de la quantité d’amine présente dans le système.

L’EDA additionnée à l’argile acide en quantités plus faibles que ou égales à la capacité d’échange cationique (C.E.C.) est exclusivement adsorbée comme ion éthylènediammonium (EDAH$_2^+$). Lors d’une addition supplémentaire de diamine le pH de la suspension monte à des valeurs alcalines, et l’espèce monoprotonée (EDAH$^+$) est le principal cation compensateur de charge.

L’évaporation à température ordinaire des systèmes “montmorillonite–H–EDA–H$_2$O” ou “montmorillonite–EDAH$_2$–EDA–H$_2$O” contenant 300 me d’EDA/100 g d’argile ne provoque pas de perte d’azote, contrairement au dégazage sous vide poussé (10$^{-5}$ mm Hg). Néanmoins des molécules d’EDA en excès par rapport à la C.E.C. sont retenues à la surface argileuse, aux dépens de molécules d’eau, par des ponts hydrogène asymétriques forts entre leurs groupes NH$_2$ et les groupes NH$_3^+$ des ions EDAH$^+$. Lors du chauffage sous vide jusqu’à 160°C le contenu en azote continue à décroître, mais se maintient toujours à un niveau sensiblement supérieur à la valeur de la C.E.C., tandis que tous les groupes NH$_3^+$ restent engagés dans des liaisons hydrogène. On suggère qu’un processus de “condensation” a lieu, impliquant le dégagement de molécules d’EDA et donnant naissance à des associations “polymériques” entre la diamine protonée et non protonée.

Le lavage à l’eau distillée des suspensions d’argile ne déplace pas non plus complètement l’excès d’EDA; cela en raison de l’équilibre existant entre les espèces ioniques en solution (EDAH$_2^+$ et EDAH$^+$) et à la surface argileuse. Il semble que ces espèces sont adsorbées préférentiellement sous forme d’associations “trimériques” dans lesquelles deux des quatre groupes NH$_3^+$ sont liés par ponts hydrogène aux groupes NH$_2$.

Après chauffage à 200°C, l’azote retenue à la surface de l’argile s’y trouve principalement sous forme d’ions NH$_4^+$. La formation d’ammonium est favorisée par la présence d’EDA en excès, et est considérablement plus rapide que dans des systèmes de montmorillonite contenant de l’EDA coordonnée aux ions Cu$^{2+}$.


Das dem sauren Ton zugefügte EDA in Mengen, die das Kationenaustauschvermögen (K.A.V.) nicht überschreiten, wird ausschließlich als Ethyldiammonium-ion (EDAH$_2^+$) adsorbiert. Bei weiterer Zugabe von Diamin steigt die Suspensions-pH zu alkalischen Werten, und die monoprotonierte Art (EDAH$^+$) ist das hauptsächlichste ladungsaußergleichende Kation.


Es gelingt auch nicht, den Überschuss an EDA durch Waschen der Tonsuspensionen mit destilliertem Wasser ganz zu entfernen; dies als Folge des Gleichgewichts, das zwischen den Ionenarten in der Lösung (EDAH$_2^+$ und EDAH$^+$) und an der Tonoberfläche besteht. Es scheint, dass diese Arten vorzüglich als “trimmerische” Assoziationen, in denen zwei der vier NH$_3^+$-gruppen durch Wasserstoffbrücken mit den NH$_2$-gruppen verbunden sind, adsorbiert werden.

Nach Erhitzen auf 200°C ist der auf der Tonoberfläche zurückgehaltene Stickstoff hauptsächlich in der Form von NH$_4^+$-ionen. Die Ammoniumbildung wird durch die Anwesenheit von Überschuss–EDA beginnist und ist bedeutend schneller als in Montmorillonitsystemen, die mit Cu$^{2+}$-ionen koordiniertes EDA enthalten.

Резюме — Для определения количества амина в агрегате, изучалось каким образом этилендиамин (EDA) адсорбируется из водных растворов водородным и этилендиаммониевым монтмориллонитом.

EDA добавленный к кислой глине в количестве ниже или равном катионообменной способности
(C.E.C.) был адсорбирован исключительно в виде иона этилендиамиона (EDAH\(^2^+\)). При дальнейшем добавлении диамина, pH взвеси поднялся до щелочного значения и «монопротонированный» ряд (EDAH\(^+\)) стал главным балансирующим катионом заряда.

Выпаривание при комнатной температуре агрегатов «EDA–H–монтмориллонита–H\(_2\)O» или «EDA–EDAH–montmorillonite–H\(_2\)O», содержащих 300 пе глины EDA/100 г не ведет к потере азота, но дегазирование при высоком вакууме (10\(^{-4}\) мм Hg) ведет. Несмотря на это, избыток молекул EDA относительно C.E.C. был сохранен на поверхности глины за счет водяных молекул вследствие сильной асимметричной водородной связи между группами NH\(_2\) и NH\(_2^+\) ионов EDA\(^+\). При нагревании до 160\(^\circ\)C под вакуумом содержание азота добавочно понижается, но все же остается на значительно высшем уровне, чем значение C.E.C., все группы NH\(_2^+\) остаются в сильной водородной связи. Предполагают, что происходит процесс конденсации, заключающийся в себе эволюцию молекул EDA и вызывающий «полимерные» ассоциации между «протонированным» и «непротонированным» диамином.

Промывка суспензии глины дистилированной водой также полностью не удаляет избытка EDA вследствие равновесия существующего между ионными группами в растворе (EDAH\(^2^+\) и EDAH\(^+\)) и на поверхности глины. Очевидно, эти группы избирательно адсорбируются как «тримерные» ассоциации в которых две из четырех групп NH\(_2^+\) имеют водородную связь с группами NH\(_2\).

После нагревания при 200\(^\circ\)C, азот задержанный на поверхности глины был главным образом в виде ионов NH\(_2^+\). Образование аммония усилилось присутствием избытка EDA и было значительно быстрее, чем в агрегатах монтмориллонита содержащих EDA координированных с ионами Cu\(^2^+\).