# THE ADSORPTION OF SOME ORGANIC COMPOUNDS, ESPECIALLY HERBICIDES, ON CLAY MINERALS

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# LIST OF SYMBOLS

| | |
|---|---|
| A | adsorbed quantity expressed in the cation exchange capacity as a unit |
| b | crowding factor |
| $c^+$ and $c^-$ | concentrations of $c^+$ and $c^-$ ions respectively |
| $c_0$ | saturation concentration |
| c.e.c. | cation exchange capacity |
| d | distance defined by equation [26] |
| D | thickness of the liquid layer |
| E | adsorption energy |
| $E_1$ | mean molar heat of adsorption for the first adsorption layer |
| $E_L$ | molar heat of crystallization |
| f(g) | factor defined by equation [16] |
| K | constant defined by equation [27] |
| g, $g^+$ and $g^{++}$ | concentrations of g molecules, $g^+$ or $g^{++}$ ions respectively |
| p | polarization |
| 2r | thickness of the adsorbed layer of g ions |
| x | adsorbed quantity; also distance to the surface |
| $x_{c=30}$ | adsorbed quantity at an equilibrium concentration of 30 $\mu$moles per l |
| $x_m$ | maximum amount which can be adsorbed in the first adsorption layer |
| X | distance parameter defined by equation [5] |
| subscript e | refers to the equilibrium solution |
| subscript s | refers to the neighborhood of the surface |
| subscript st | refers to the quantity adsorbed in the Stern layer |
| $\alpha$ | polarizability |
| $\beta$ | $8\pi F^2/1000\varepsilon RT$ in which F is the faraday |
| $\Gamma^+$ and $\Gamma^{++}$ | adsorbed quantities of monovalent and divalent cations in the double layer |
| $\Gamma^-$ | (negatively) adsorbed quantity of monovalent anions in the double layer |
| $\delta$ | distance defined by equation [5] |
| $\varepsilon$ | dielectric constant |
| $\varkappa$ | defined by $\varkappa^2=\beta I$, in which I is the ionic strength of the equilibrium solution |
| $\Sigma_s$ | total concentration of ions close to the surface |
| $\Sigma_e$ | total concentration of ions in the equilibrium solution |
| $\sigma$ | surface charge density |
| $\sigma_g{}^+$ | charge of the adsorbed quantity of g ions |
| $\varphi_g$ | adsorption energy for g ions in addition to Coulombic forces |
| $\psi$ | potential |
| $\psi_d$ | potential at a distance $2r + d$ from the surface |
| $\psi_r$ | potential at a distance r from the surface |

# SUMMARY

A critical review of the existing literature on adsorption of organic compounds on clay minerals indicates that in many cases the measurements cannot be interpreted unambiguously, because various important factors were not taken into account and because of the complicated nature of the system studied. Especially the information gained from X-ray studies appears to be onesided and may have lead to misinterpretation. In the present study a number of adsorption isotherms were determined of various organic materials, mainly herbicides, on different clay minerals. The adsorption of the compounds studied appears to be strongly dependent upon salt concentration and pH. At very low pH all compounds are adsorbed rather strongly. In slightly basic environment the anionic substances are adsorbed negatively whereas the non-ionic compounds show a moderate adsorption. Methylene blue is invariably strongly adsorbed, in several cases reversal of charge of the clay mineral was observed. In order to compare the adsorption of organic anions with inorganic anions some experiments with $I^{131}$- and Cl-ions were included.

With regard to the reaction mechanism in aqueous environment several types of adsorption should be distinguished. When the herbicides are adsorbed as ions, they are present in a diffuse layer. In several cases this type of adsorption may be treated quantitatively, e.g. with the Gouy theory. Generally non-Coulombic forces play an important rôle in addition to Coulombic forces. The adsorption of the substituted triazines and ureïdes (weak bases) is mainly caused by the adsorption of positively charged ions formed through association with protons. The calculated value of the negative adsorption of organic anions on the negatively charged clay surface proved to be in agreement with experimental values. The observed positive adsorption of organic anions on the clay mineral illite took place on the positively charged edges of the clay platelets. The organic acids studied may also be adsorbed in undissociated form. From the experimental observations it may be concluded that in agricultural practice the accumulation of certain herbicides in soil is possible.

# PART I. EXPERIMENTAL DATA

## 1. INTRODUCTION

The interaction between clay minerals and organic compounds has been a subject of research since several years. The interest in this interaction stems from the expectation that the adsorption of the organic matter fraction in the soil on the mineral particles would contribute to the physical stability of soil aggregates. Thus one has attempted to isolate these organic matter fractions from the soil, and has subsequently studied the effect of their addition to the purified mineral fraction. As it became clear that the organic compounds in the soil system form a more or less continuous series of polymers with increasing molecular weight, the members of this series possibly being polymerized or depolymerized during isolation, the interest in the interaction between clay and organic compounds from the soil itself has faded. Instead it seems more promising to study the interactions between clays and certain synthetic, well-defined compounds, which could then be used as a model for the processes occurring in field soils.

Aside from these model substances a growing interest has arisen in the behavior in soils of organic additives which are employed in agricultural practice. Of these compounds the herbicides and pesticides and the 'soil conditioners' are of primary concern. The latter can be instrumental to the improvement of the soil structure, as after treatment a more favorable aggregation may result. In this connection the mechanism of binding between clay and organic material is quite important.

The interest in the adsorption of herbicides and pesticides stems from the expectation that, although the amounts applied are generally small, a possibility of accumulation over several years should be considered. At the same time the adsorption characteristics are of concern when considering the effective concentration for a given application.

Although this research was instigated to obtain general information regarding the factors which are of primary concern for the adsorption of organic materials on clay minerals, the chemicals studied were mainly herbicides. Especially with regard to herbicides quantitative data are important.

# 2. STRUCTURE OF CLAY MINERALS

For the interpretation of adsorption-phenomena on clay minerals some insight in the structure of these minerals is essential. Therefore a short review of the information available on this structure is given first.

The clay minerals used viz. montmorillonite, illite and kaolinite consist mainly of sheets of aluminum and oxygen and sheets of silicon and oxygen (26). The former comprise octahedrons, the corners of which are formed by the oxygen atoms and the centres by the aluminum atoms. On the other hand the silica sheets are composed of tetrahedrons, again having oxygen atoms on the corners; the centres, however, are occupied by silicon atoms. The silica-tetrahedrons share corners with each other, terminal oxygens (at the edges and lines of fracture) being present as hydroxyl-groups. The alumina-octahedrons also share corners, and depending on the type of clay mineral either one-third or two-thirds of the oxygen atoms are present as hydroxyl-groups. The clay mineral crystals now consist of a combination of silica and alumina sheets, either simply alternating (1:1 type clay minerals, e.g. kaolinite) or in the order 'silica-alumina-silica' (2:1 type, e.g. montmorillonite, illite). The silica and alumina sheets share corners.

Clay minerals are charged negatively, mainly on account of isomorphous substitution, e.g. Si- by Al-ions. The charge can, however, also be caused by ionisation of the AlOH- and SiOH-groups, present mainly on the edges. On account of the latter mechanism the charge depends upon the pH, with regard to both sign and magnitude. In acid environment, when the exposed OH-groups tend to become positive, both positive and negative charges can exist simultaneously, at high pH the OH-groups will become negatively charged. There is no unanimity of opinion about the relative magnitude of the two charging mechanisms. FRIPIAT (21) and GENTILI (22) are of opinion that the isomorphous substitution plays an important part in the case of montmorillonite only; in the case of kaolinite FRIPIAT ascribes the negative charge entirely to ionisation. SCHOFIELD (51) and CASHEN (12), although recognizing the importance of ionisation charge for the clay mineral kaolinite, are of opinion that with illite and montmorillonite ionisation will only occur on the edges of the particles to a minor extend and that isomorphous substitution is the predominant source of negative charges in all clays.

Quantitative data concerning the cation exchange capacity (c.e.c.) of the clays studied are given in table I-1. In accordance with the foregoing the value of the positive charge at low pH values cannot be given exactly. FRIPIAT (21) reports an adsorption of 1 to 4 μeq. Cl-ions per g of kaolinite; for the other clay minerals probably lower values should be expected.

With montmorillonite and illite the thickness of the elementary plate is approximately 10 Å, the length and breadth of the platelets vary from 100 Å to 1000 Å. In the case of kaolinite the thickness of the elementary plate is approximately 6 Å, whilst the

TABLE I-1. Some general properties of clay minerals

| | Montm. | Illite | Kaolinite |
|---|---|---|---|
| Total surface, $cm^2/g$ | 4 to 9 $\times 10^6$ | 0.5 to 3 $\times 10^6$ | 0.04 to 0.8 $\times 10^6$ |
| Neg. charge of basal plane, meq.*/$cm^2$ | $-1 \times 10^{-7}$ | $-3 \times 10^{-7}$ | $-2 \times 10^{-7}$ |
| Neg. charge of basal plane, meq./g | 0.5 to 1 | 0.15 to 0.6 | 0.01 to 0.2 |
| Type of swelling | expanding | non-expanding | non-expanding |

*$10^{-7}$ meq. = 9.57$\mu$C.

length and the breadth vary from 1000 Å to 10000 Å or even larger. Although in dry condition the particles of all clays do appear in units of 50 to 2000 Å thick (thus consisting of several plates) there is quite a difference between the montmorillonite on one hand and illite and kaolinite on the other hand. This is evidenced by the swelling characteristics of the different clays. X-ray determination of the basal spacing (distance between centres of adjacent clay plates) has shown that with the entry of water, montmorillonite particles are often separated into individual platelets which may swell to considerable distances from each other; this has given rise to the use of the name 'expanding lattice'. On the other hand illites and kaolinites swell only between larger units and accordingly total swelling is much less than for montmorillonite. These clays are characterized as 'non-expanding lattice' clays. Partly in consequence of the different character between the individual plates with regard to the entry of water, the c.e.c. is lower for illite than for montmorillonite. Also the surface area of the minerals is dependent upon the type of the lattice. In theory the area of the planar surfaces of montmorillonite (i.e. not counting the edge-surface) should be about 800 $m^2/g$. This agrees with experimental data, which indicate a total surface area of 700–900 $m^2/g$ in most cases, although 400 $m^2/g$ was also found. For illite the theoretical value should be 800 $m^2/g$, divided by the number of sheets per crystal. Experimental values vary between 50 and 250 $m^2/g$. Kaolinite, containing usually a much higher number of plates per crystal, exhibits a much lower value of the specific surface area.

# 3. REVIEW OF LITERATURE ON ADSORPTION

Although a considerable amount of data is available from the literature concerning the adsorption of organic materials by clays, these experiments must be scrutinized in order to establish their significance. Many of the observations were made under exclusion of water and give little evidence with regard to what may happen in the wet system as occurs in natural soils. At the same time the materials employed were often rather poorly defined thus making the interpretation very difficult.

In order to establish the significance of different sources of literature concerning adsorption, a division was made on the basis of the measuring technique employed. Thus the results obtained by infrared analysis and X-ray analysis will be treated seperately from the information gained from the determination of adsorption isotherms.

## 3.1. RESULTS OBTAINED FROM INFRARED ANALYSIS

Infrared measurements require working in an infrared transparent environment or drying of the adsorption complex. This restricts the possibilities of this technique considerably. In 1957 **HOLMES** and **TOTH** (31) examined the adsorption of a half-amide, half-ammonia salt of a copolymer of methyl vinyl ether and maleïc acid in nujol on montmorillonite, illite and kaolinite. The absorption-bands in the infrared region corresponding to free OH-groups of the clay, disappear at very high concentrations of the organic compound mentioned, indicating adsorption. **MORTENSEN** (42) found that in case of adsorption of HPAN (hydrolyzed polyacrylonitrile) on kaolinite H-bonds are formed. Infrared analysis has proved to be extremely useful for the evaluation of the structure of the organo-clay compounds. **GENTILI** (22) thus could prove that e.g. benzoic chloride was not adsorbed on dry clay, but that instead a chemical reaction occurred. In respect of the bonding mechanisms in aqueous environment, however, this method does not provide any new points of view.

## 3.2. RESULTS OBTAINED FROM X-RAY ANALYSIS

In 1934 already **HOFMANN** et al. (30) treated montmorillonite and kaolinite with alcohol, acetone and ether and measured the basal spacing of treated and untreated clay by means of X-ray. The observed increase in basal spacing of the treated clay indicates that the organic compounds had found a place between the elementary plates of the montmorillonite. The basal spacing of kaolinite, although the sample appeared to be swollen, remained unchanged.

As a matter of fact this should be expected with a non-expanding lattice. The adsorption takes place on the outsides of the crystals only, whereby the distances between the elementary plates remain unaltered. It is exactly this distance which is determined by means of X-ray. Thus with clay minerals with a non-expanding lattice it is in principle impossible to ascertain by means of X-ray whether organic compounds are being adsorbed on the basal plane or on the edges. This is only feasible in the case of clay minerals with an expanding lattice. This may be the reason that many investigators have restricted their X-ray research with organic compounds to the study of expanding lattice clays. It is obvious that generalization to the adsorption of these organic compounds to non-expanding clay minerals, based on their behavior on montmorillonite, is not acceptable.

Notwithstanding the fact that X-ray analyses are usually performed on dry samples, many authors tend to overinterprete the data, and to extrapolate them to adsorption in aqueous environment. This misappreciation had been enhanced by a publication by HENDRICKS (29) in 1941. This author prepared an H-montmorillonite and titrated it with an aqueous solution of basic compounds such as benzidine, piperidine and aniline until a pH of 7 was reached. The c.e.c. thus obtained agreed with the known value of the c.e.c. Consequently adsorption on the negative basal plane had been proved. After drying it now appeared that the basal spacing had increased; this increase in spacing was retained in the presence of 70% of water. Thus it was concluded that the organic compound had been adsorbed on the negatively charged basal plane and that this adsorption was already present at a considerable moisture content. Although this conclusion was undoubtedly correct, because the compound concerned was a basic compound which indeed replaces the exchangeable cations, it was erroneously concluded by other authors that, in general, an increase in basal spacing observed in dry condition will imply that the adsorption was already present at a considerable moisture content.

## 3.3. ADSORPTION ISOTHERMS

A fair amount of data relating to the adsorption of organic compounds from aqueous solution on clay is available. Because of the dissociation of some of these compounds in aqueous solution, a division is made according to non-ionic compounds, cations and anions.

### 3.3.1. *Non-ionic compounds*

GREENLAND (24) examined the adsorption of sugars on montmorillonite in 1954. GREENLAND's measurements show that methylsugars are adsorbed more strongly than the corresponding ordinary sugars. LYNCH, WRIGHT, HEARN and COTNOIR (37) determined the adsorption of cellulose-derivates, methylcellulose, polysaccharides, sucrose, etc. on H-montmorillonite (or probably Al-montmorillonite). Often the amount of adsorption was a function of the type of clay mineral and the nature of the adsorbed cations.

### 3.3.2. *Organic cations*

GRIM, ALLAWAY and CUTHBERT (25) ascertained in 1947 that small organic cations were adsorbed in amounts up to the c.e.c. Large organic cations were adsorbed in excess of the c.e.c. They assumed that enclosure of the inorganic cations originally present, as well as adsorption of the added bromide ion could occur. Both assumptions were verified experimentally. Excellent material concerning the exchange of simple amine-ions with Na- and Ca-ions on montmorillonite was published by SLABAUGH and KUPKA (56) and by COWAN and WHITE (13). Apparently this exchange is in accordance with the cation exchange properties of clay. ROBERTSON and WARD (49) as well as FAIRBAIRN and ROBERTSON (20) developed a method to determine the c.e.c. of clay with the aid of methylene blue. Their method of determination of the c.e.c. of clay assumes that a proportionality exists between the amount of methylene blue adsorbed in the presence of a small excess of methylene blue in solution and the c.e.c. of the clay. This assumption is not supported by theoretical considerations (cf. section 3.1., Part II of this publication). Also PETER and MARKERT (46) examined the adsorption of methylene blue. They found that in soils with a low c.e.c. the adsorption is in accordance with Freundlich isotherms. In fact this is in conflict with the assumed proportionality between the amount adsorbed and the c.e.c.

Proteins behave like cations when the pH is lower than the isoelectric point. Articles on the adsorption of these compounds were published by ENSMINGER and GIESEKING (17), by LYNCH, WRIGHT, HEARN and COTNOIR (37) and by MCLAREN, PETERSON and BARSHAD (39). All of them found that the adsorption was dependent upon the isoelectric point and the pH. Owing to the nature of the material the interpretation of the experiments is often rather difficult, whereas calculations are generally impossible.

### 3.3.3. *Organic anions*

WALLACE and LUNT (58) investigated the adsorption of some iron-, zinc- and manganese-chelates. They presumed that FeEDTA appears as a monovalent anion between a pH of 3.6 and a pH of 8. This compound proved to be strongly adsorbed. Particularly with montmorillonite the adsorption was much larger than the expected number of positive charges on the clays. It appears from their data that the question of the adsorption of chelates is very much involved and has in no way been clarified.

Quite a number of articles were published on the synthetic polyanions to which the soil conditioners belong. RUEHRWEIN and WARD (50) determined for HPAN (hydrolyzed polyacrylonitrile) an adsorption of 2 meq. per 100 g montmorillonite. MARTIN and ALDRICH (38) ascertained that IBMA (the copolymer of isobutylene and the half amide- half ammonium-salt of maleïc acid) was adsorbed to a lesser degree on Na- and K-clays than on Ca-clays. MORTENSEN and MARTIN (40) therefore concluded that there exist a binding of the type $\text{clay}^{-}\ldots \text{Ca}^{++}\ldots {}^{-}\text{OOCR}$. The effect of the exchangeable cations is also evident in MORTENSEN's work (41, 42); this author found that HPAN adsorbed to a greater extent on a clay saturated with polyvalent ions than on a clay with monovalent ions. The order was $\text{Th}^{++++} > \text{Ca}^{++} > \text{Ba}^{++} > \text{H}^{+} > \text{NH}_4^{+} > \text{K}^{+} > \text{Na}^{+}$, so both lyotropic and valence effects are present. MORTENSEN voices the opinion that the adsorption is correlated with the zeta potential of the clay minerals. KHAN (33), EVANS and RUSSELL (19) examined the adsorption of humic acids (soil extracts). Apart from the adsorption via the positive edges they also assume a binding via the di- and tri-valent inorganic cations present in the system. VAN OLPHEN (44) suggests the same mechanism for the adsorption of tannins by montmorillonite.

From GREENLAND's tables (24) it appears, that with the adsorption of gluconic and glucuronic acid on montmorillonite sometimes also negative adsorption occurs, although this was not recognized by GREENLAND.

# 4. EXPERIMENTAL

## 4.1. GENERAL CONSIDERATIONS

In view of the mentioned ambiguity of methods other than the determination of adsorption isotherms, the latter method was chosen to study the adsorption of herbicides and some related compounds on clays.

Presumably the adsorption is influenced by several factors, which are discussed in detail in Part II of this study. From these considerations it follows that the behavior of ionic compounds should in first approximation comply with the classical theories of the diffuse layer formed on charged surfaces. Especially the negative adsorption of anions by the negatively charged clay surface should follow the theory quantitatively, thus varying with the electrolyte content, valence of the dominant cation in the system and the specific surface area of the clay.

Positive adsorption of anions may occur if positively charged sites are present on the edges of the clay plates. Because of the irregularities of the edges and the ease of dehydration of the anions this adsorption will be strongly preferential, the preference in comparison to other anions being due to the presence of non-Coulombic attraction forces between the clay edges and anions. The clay mineral will in this case be an important variable.

The positive adsorption of organic cations should be also highly preferential due to non-Coulombic forces and should again be dependent upon the electrolyte concentration and the nature of inorganic cations present. Reversal of charge by organic cations seems a logical consequence of strong and specific attraction forces. The adsorption of non-ionic organic compounds, as a result of Van Der Waals and other non-Coulombic forces, will be important only if these compounds have a large dipole moment or an aromatic structure.

In accordance with these expectations adsorption isotherms were determined at several values of the electrolyte concentration and in the presence of mono-, di- and tri-valent inorganic cations.

Because the pK value of several herbicides is in the neighborhood of existing pH values in soils, a strong influence of the pH on the adsorption should be expected. In the first place the effect of uncharged molecules at pH values below the pK of the organic acids should be considered, especially if a strong non-Coulombic interaction between uncharged molecules and clay would exist. Since some of the non-ionic compounds studied (e.g. substituted ureïdes and triazines) exhibit the tendency to adsorb protons at low pH values, increased adsorption of these components (as cation) should also be expected at decreasing pH. Finally the existence of positively charged sites on the clay mineral edges will also be dependent on the pH. Accordingly there is little doubt that the pH must be a major variable in the adsorption phenomena studied.

The effect of very high salt concentrations (above 1N) may be treated as a separate phenomenon. The double layer is virtually non-existent under these conditions (the surface charge density of clays being fairly constant). At these high concentrations the activity coefficients of the organic compounds should be influenced considerably, leading to changes in the adsorption characteristics.

The above considerations indicate the necessity to characterize the experimental conditions under which the isotherms are determined with regard to electrolyte concentration and pH. The experiments were conducted in such a manner that the effects of these factors could be evaluated as far as possible. In the present study only fairly well defined clays were used, whereas cationic and anionic composition and the pH of the suspension were rigidly controlled. As clay minerals a montmorillonite, illites and kaolinites, all in homoionic form (Na or Ca) were chosen. These materials constitute a representative sample of the range of variation to be expected in practice with regard to surface area, mineralogical composition, swelling characteristics and charge distribution (cf. table I-1).

## 4.2. Materials and methods

### 4.2.1. *Clay minerals*

The experiments were made with the fraction $<2\mu$ of the following clay minerals: montmorillonite (Bentonite from Osage, Wyoming), illite (Grundite company, samples L and M), kaolinite (Drybranch and Dixieclay) from the U.S.A., illite (Winsum) from the Netherlands and kaolinite (Zettlitz) from Czechoslovakia. For general properties and experimental data reference is made to the tables I-1 and I-2. The clays were used as Na-, Ca-, or Al-clays. Unless otherwise stated the anion present was chloride. The preparation of the homoionic clays and the removal of salt from the clay suspensions were done according to the method of Bolt and Frissel (8). This method consists of the removal of carbonates and exchangeable Al by means of H-resin treatment at a pH of 3, and saturation with the desired cation by means of column or batch treatment with the appropriate resin (in some cases with concentrated salt solutions). The degree of saturation of the clays with the desired cations always exceeded 98.5 %. If necessary, organic material was removed prior to resin treatment with $H_2O_2$.

Table I-2. Composition and some other properties of the clays studied

| Type of clay | c.e.c. meq./g | Surface area $\text{cm}^2$/g ($\times 10^6$) | Illite % | Montm. % | Kaolinite % | Quartz % |
|---|---|---|---|---|---|---|
| Montm. (Wyoming) | 0.93 | 9.0 | – | 97 | – | 2–3 |
| Illite (Grundite, L) | 0.19 | 2.5 | 95 | – | trace | 3–5 |
| Illite (Grundite, M) | 0.25 | 2.8 | | | | |
| Illite (Winsum) | 0.40 | 3.0 | 80 | 5–10 | 5 | 5–10 |
| Kaolinite (Dixieclay) | 0.04 | 0.4 | – | – | 100 | – |
| Kaolinite (Drybranch) | 0.06 | 0.5 | – | 5 | 95 | – |
| Kaolinite (Zettlitz) | 0.05 | 0.6 | trace | – | 98 | trace |

The specific surface of the clay was determined by ethylene glycol retention according to the method of Dyal and Hendricks (15) and Bower and Goertzen (9). The mineralogical composition of the clay samples was determined by means of X-ray diffraction.*

*The composition was kindly determined by Dr. J. Ch. L. Favejee.

### 4.2.2. *Organic compounds*

The organic compounds* used included the acids 2,4–D, 2,4,5–T, MCPA, DNC, DNBP, picric acid and picrolonic acid, the base methylene blue, and the very weak bases simazine, chlorazine, trietazine, CMU and DCMU. Table I-3 shows the trade name together with the chemical name. Often the trade product consists of the Na-, $NH_4$-, or triethanolamine-salt, whereas on behalf of the formulation other components have been added. Although in the description of the experiments the trade name is used, the measurements were made with the unformulated compounds. The chemicals were purified by recrystallization if necessary. The melting points are given in table I-4. Concentrations were determined by measuring the extinction, employing a Zeiss U.V. spectrophotometer, type PMQ II. Table I-4 shows the wavelength used. Most compounds were measured in the presence of a $NH_4Cl/NH_4OH$ buffer, pH 8.3. The solutions were prepared with demineralised water having a specific resistance of $3 \times 10^6$ Ωcm and a dry matter content of about 0.2 mg per l. The pK of the various compounds was determined by plotting the extinction as a function of the pH at a suitable wavelength. The pK was then obtained as the pH at the inflection point of the S-shaped curve. (The pK is defined here as the pH at which equal amounts in moles per unit volume of the dissociated and associated form under consideration are present). It appeared to be difficult to find a suitable wavelength for the triazines, because the second proton was already adsorbed before all the neutral molecules had disappeared. To avoid this difficulty, the A.G. Geigy employed, a wavelength at which the monovalent and divalent ions have equal extinctions.

TABLE I-3. Trade name and chemical name of the organic compounds

| | |
|---|---|
| 2,4–D | 2,4-dichlorophenoxy acetic acid |
| 2,4,5–T | 2,4,5-trichlorophenoxy acetic acid |
| MCPA | 2-methyl-4-chlorophenoxy acetic acid |
| DNC | 4,6-dinitro-o-cresol |
| DNBP (Dinoseb) | 4,6-dinitro-2-secundary-butylphenol |
| Picric acid | 2,4,6-trinitrophenol |
| Picrolonic acid | 4-nitro-3-methyl-1-p-nitro-phenylpyrazolone-5 |
| Simazine | 2-chloro-4,6-bis (mono ethylamino)-s-triazine |
| Chlorazine | 2-chloro-4,6-bis (di ethylamino)-s-triazine |
| Trietazine | 2-chloro-4-di ethylamino-6-mono ethylamino-s-triazine |
| CMU (Monuron) | 3-p-chlorophenyl-1,1-dimethylurea |
| DCMU (Diuron) | 3-(3,4-dichlorophenyl)-1,1-dimethylurea |
| Methylene blue | methylene blue |
| HPAN | hydrolyzed polyacrylonitrile |

### 4.2.3. *Methods*

The technique employed depended on the salt concentration. Na-clay and Ca-clay can be centrifuged clear at salt concentrations in excess of 0.04 N NaCl and 0.001 N $CaCl_2$ respectively. For these systems 5 ml of the desired clay suspension were pipetted into a volumetric flask with ground glass stopper, while adding a sufficient amount of acid, base, and/or salt to reach the required salt concentration and pH. (The cations of the salt added invariably correspond with the counter ions of the clay mineral). Thereupon the solution with the organic compound was added by pipette, and the suspension was made up to volume. Depending on conditions the system was equilibrated by shaking

*The chemicals were kindly supplied by the following companies: N.V. Philips-Duphar, Amsterdam, Netherlands: 2,4–D, 2,4,5–T and MCPA; N.V. Fabriek voor Chemische Producten, Vondelingenplaat, Netherlands: DNC and DNBP; J. R. Geigy A.G., Basel, Switzerland: simazine, chlorazine and trietazine; E.I. Du Pont De Nemours and Co (Inc.) Wilmington Del., U.S.A.: CMU and DCMU.

**Table I-4.** Some properties of the organic compounds, as determined

| Trade name | Meltingpoint (corrected) °C | Wavelength in mμ | | $pK_1$* | $pK_2$* |
|---|---|---|---|---|---|
| | | Determ. of conc. | Determ. of pK | | |
| 2,4–D | 139–141 | 220 | 209 | 2.80 | |
| 2,4,5–T | 155–156 | 220 | 215 | 2.65 | |
| MCPA | 119–121 | 220 | 206 | 2.90 | |
| DNC | 86 | 400 | 400 | 4.35 (4.35) | |
| DNBP | 37– 39 | 425 | 425 | 4.35 | |
| Picric acid | 122 | 355 | 355 | 0.40 (0.38) | |
| Picrolonic acid | 120 | 350 | 350 | 0.50 | |
| Simazine | 229–231 | 220 | 225 (254) | 1.4 to 1.6 (1.65) | (approx. 0) |
| Chlorazine | 15– 18 | 240 | 205 | 1.5 to 1.7 (1.74) | |
| Trietazine | 102–103 | 235 | 230 (264) | (1.88) | (approx. 0) |
| CMU | 173–174 | 244 | 205 | –1 to –2 | |
| DCMU | 158–159 | 244 | 205 | –1 to –2 | |
| Methylene blue | – | 668 | – | | |

* Values in parenthesis indicate data obtained from manufacturer or literature.

for a certain period, usually 4 hrs for systems containing low molecular weight organic compounds, 48 hrs for systems containing polymers, 1 hr for systems at a pH below 3 (because of decomposition of clay at low pH). Then the equilibrium liquid was separated off by centrifugation.

In the case of low salt concentrations dialysis was employed. The suspension to be analysed was weighed into a weighing flask of 50 ml. Subsequently a small bag of dialysis tubing (A. H. Thomas Co, Philadelphia, U.S.A.), containing 10 ml of destilled water, was brought into the suspension and the system was gently shaken for 30 hrs.

After equilibration, the concentration of the organic compound and the pH were determined in the centrifugate or dialyzate, resp. Blank determinations (viz. clay in absence of organic compound and organic compound in absence of clay) were always included. In case of the dialysis the blank was also employed to determine the salt concentration of the system, which was unknown in this case. During equilibration and determination of the concentration the temperature was kept constant between 18 and 20°C. When calculating the adsorption the dry volume of the clay was taken into account.

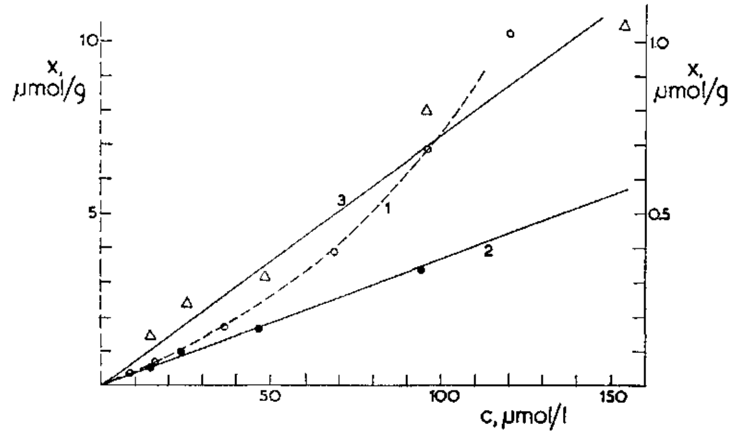
## 4.3. RESULTS

The experimental data are presented largely in the form of hand drawn curves through observed points. Deviations between experimental points and curves were less than 5% unless stated otherwise. The number of points varied for the different experiments, but was never less than five, distributed fairly homogeneously over the curve; each point was the mean value of duplicate determinations. The amounts adsorbed are always given in μmoles per g of adsorbent, including the ionic adsorbates.

### 4.3.1. *The adsorption of CMU and DCMU*

CMU and DCMU are closely related substituted ureïdes, which are practically undissociated in neutral environment. The figures I-1, -2 and -3 comprise various adsorption curves as a function of the equilibrium concentration, salt concentration and

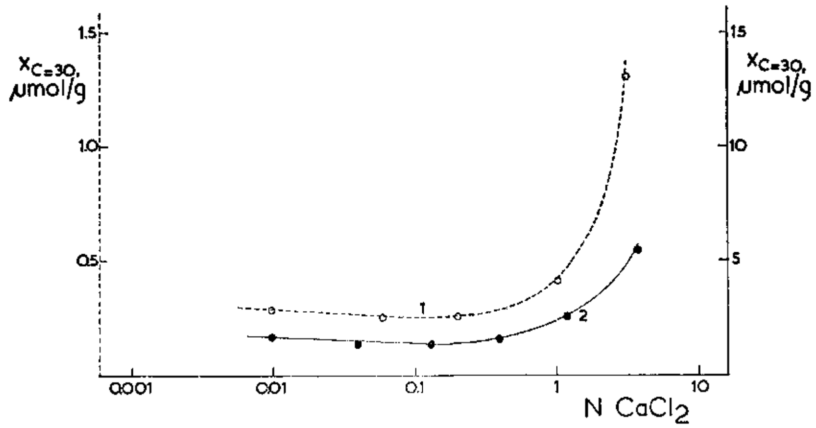
Fig. I-1. The adsorption of CMU



Curve 1: On Na-montmorillonite in 3.6 N NaCl, pH 7.0 (left-hand scale)
Curve 2: On Ca-illite (Grundite, L) in 0.06 N $CaCl_2$, pH 6.2 (right-hand scale)
Curve 3: On Na-montmorillonite in 0.06 N NaCl, pH 6.4 (right-hand scale)

the pH. Generally speaking the two compounds are adsorbed in the same way; the adsorption values of DCMU are, however, always higher than those of CMU. In figure I-1, the adsorbed quantity, x, is plotted against the equilibrium concentration, c, for different clays. Under the conditions specified it appeared that at low salt concentrations CMU exhibits a linear adsorption isotherm and at high salt concentrations a curved one. Figure I-2 shows the adsorption of DCMU on Ca-illite as a function of the salt concentration. On the ordinate the adsorbed quantity in µmoles per g at an equilibrium concentration of 30 µmoles per l is given (denoted by the symbol $x_{c=30}$). Of course it was not always possible to carry out the adsorption measurements in

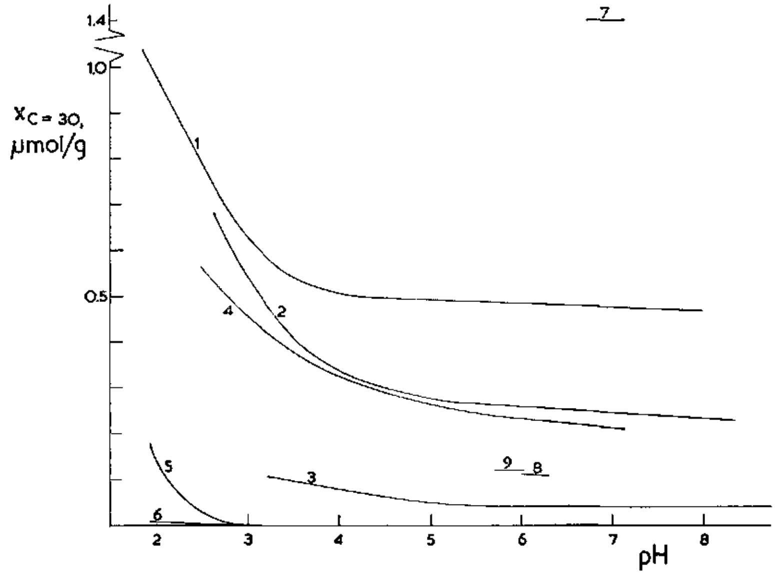
Fig. I-2. The adsorption of DCMU and chlorazine on Ca-illite (Grundite, L) as a function of the salt concentration. Equilibrium concentration organic compounds 30 µmoles per l



Curve 1: DCMU, at pH 6.0 (left-hand scale) Curve 2: Chlorazine, at pH 6.5 (right-hand scale)

such a way that the equilibrium concentration became exactly 30 μmoles per l. As most of the adsorption isotherms in the area concerned are linear a numerical correction was applied in the majority of cases. For non-linear isotherms graphical interpolation was employed. The figure shows a small influence of the salt concentration upon adsorption up to salt levels of 0.2–0.3 N; above this level the influence becomes very large. In figure I-3 the adsorption is given as a function of the pH, again for c equal to 30 μmoles per l. From the curves 4, 5 and 6 it is clear that the adsorption decreases in the entire pH range in the order montmorillonite, illite, kaolinite. Both the curves 1 and 4, as well as 2 and 8 show that DCMU is adsorbed more than CMU. With higher salt concentrations there was considerably more adsorption than with low salt concentrations (cf. curves 4 and 7, as well as 6 and 9).

FIG. I-3. The adsorption of CMU and DCMU on clay minerals as a function of the pH



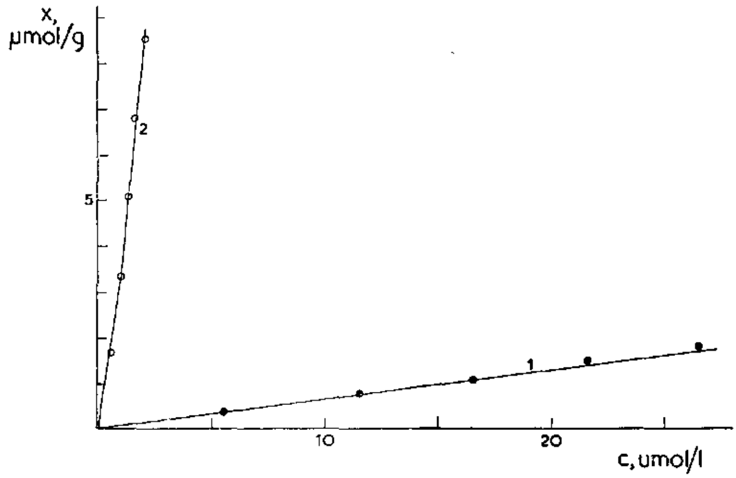
Curve 1: DCMU on Na-montmorillonite in 0.06 N NaCl
Curve 2: DCMU on Ca-illite (Grundite, L) in 0.06 and 0.2 N $CaCl_2$
Curve 3: DCMU on Na-illite (Winsum) in 0.06 N NaCl
Curve 4: CMU on Na-montmorillonite in 0.06 and 0.2 N NaCl
Curve 5: CMU on Na-illite (Winsum) in 0.06 N NaCl
Curve 6: CMU on Na- and Ca-kaolinite (Zettlitz) in 0.06 N NaCl and $CaCl_2$
Curve 7: CMU on Na-montmorillonite in 3.6 N NaCl
Curve 8: CMU on Ca-illite (Grundite, L) in 0.06 N $CaCl_2$
Curve 9: CMU on Na-kaolinite (Zettlitz) in 3.6 N NaCl

The 'curves' 7, 8 and 9 are based on single observations (in duplicate).

### 4.3.2. *The adsorption of simazine, chlorazine and trietazine*

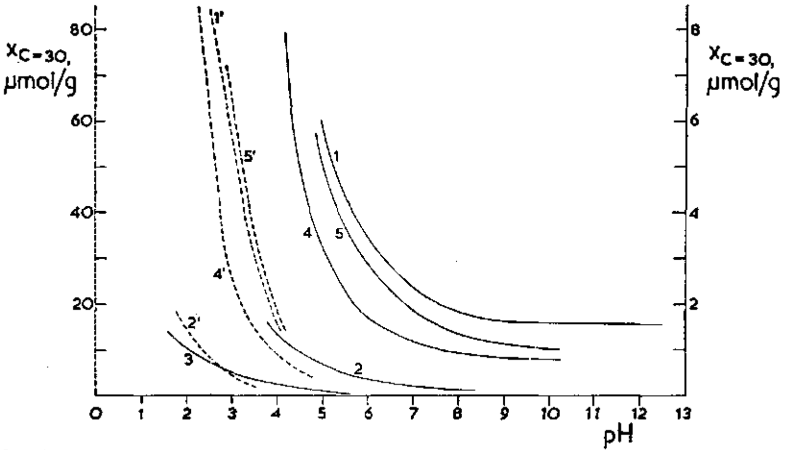
Simazine, chlorazine and trietazine are all triazines, containing two amino groups. In the figures I-2, -4 and -5 the adsorption curves are again shown as functions of the

FIG. I-4. The adsorption of chlorazine



Curve 1: On Ca-illite (Grundite, M) in 0.06 N $CaCl_2$, pH 6.7 Curve 2: On Na-montmorillonite in 0.06 N NaCl, pH 1.9

FIG. I-5. The adsorption of chlorazine, simazine and trietazine, at a salt concentration of 0.06 N NaCl, as a function of the pH



Curve 1 : Chlorazine on Na-montmorillonite (right-hand scale)
Curve 1': Chlorazine on Na-montmorillonite (left-hand scale)
Curve 2 : Chlorazine on Na-illite (Winsum) (right-hand scale)
Curve 2': Chlorazine on Na-illite (Winsum) (left-hand scale)
Curve 3 : Chlorazine on Na-kaolinite (Zettlitz) (right-hand scale)
Curve 4 : Simazine on Na-montmorillonite (right-hand scale)
Curve 4': Simazine on Na-montmorillonite (left-hand scale)
Curve 5 : Trietazine on Na-montmorillonite (right-hand scale)
Curve 5': Trietazine on Na-montmorillonite (left-hand scale)

salt concentration, equilibrium concentration and the pH. The curves shown in figure I-4 indicate that the slope of the adsorption isotherms may differ considerably, depending on conditions. At high salt concentrations chlorazine was adsorbed more strongly on Ca-illite than at low salt concentrations (cf. figure I-2). From figures I-3 and -5 it is obvious that this group of compounds, particularly in acid environment, is adsorbed far more strongly than CMU and DCMU (note the difference in the calibrations of the axis). As in 4.3.1., $x_{c=30}$ was chosen as a relative measure for the quantity adsorbed. The values for $x_{c=30}$ larger than 10 μmoles per g (cf. figure I-5) are not accurate within 5%, because of the employed extrapolation procedure. Deviations are presumably not larger than 15%. Placing the adsorption in order of decreasing magnitude, it was found again that montmorillonite>illite>kaolinite. Depending upon the pH the adsorbed quantities exceeded those of CMU with a factor between 5 and 50. The differences between chlorazine, simazine and trietazine appeared to be small (cf. figure I-5). The observed adsorption, both at high salt content and at low pH values, appeared to be fully reversible. The latter case is demonstrated in table I-5. In the presence of 50% ethanol the adsorption of simazine was almost negligeable.

TABLE I-5. Reversibility of the adsorption of chlorazine on Na-montmorillonite as a function of the pH, at a salt concentration of 0.06 N NaCl, clay concentration 0.74 g per 100 ml

| | Sample at pH 1.9 | | Same sample after bringing pH to 12.0 | | |
|---|---|---|---|---|---|
| Conc. in blank, μmole/l | Conc. centrifugate μmole/1 | $x_{c=1.6}$,* μmole/g | Conc. centrifugate μmole/1 | $x_{c=30}$, μmole/g | $x_{c=30}$, μmole/g determined from fig. I-5 |
| 51.6 | 1.6 | 6.8 | 37.6 | 1.6 | 1.6 |
| 52.3 | 1.6 | 6.8 | 37.6 | 1.6 | |

* Linear extrapolation to $x_{c=30}$, as supported by figure I-4, would indicate that at pH 1.9 $x_{c=30}$ equals approximately $1.3 \times 10^2$ μmoles per g.

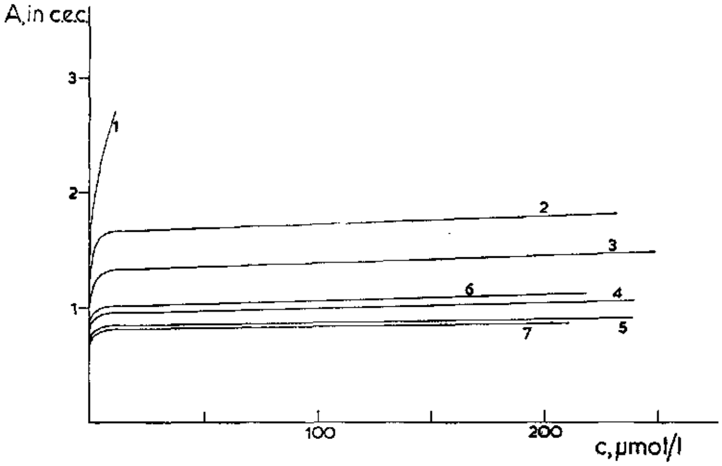
### 4.3.3. *The adsorption of methylene blue*

In contrast to the compounds reviewed earlier methylene blue usually behaves as a cation in aqueous environment. Figure I-6 shows the adsorption isotherms as functions of the cationic occupation of the clay and of the salt concentration. The adsorbed quantity of the methylene blue cations, A, is given on the ordinate in units of the c.e.c., thus allowing a comparison between the different clay minerals. For A equal to unity, the adsorption thus equals the exchange capacity of the clay. In most cases the adsorbed quantities exceeded the c.e.c. In order to make a comparison with previous experiments it should be remembered that the c.e.c. of the montmorillonite amounted to 0.93 meq. per g. For A equal to 1.5 the adsorbed quantity thus equals about 1400 μmoles per g. Because of the observed sensitivity towards the salt concentration, even at 0.1 N NaCl (cf. figure I-6) it was checked whether the order of addition of salt and methylene blue made any difference (cf. table I-6). The results show that this is only of minor importance for Al-montmorillonite, and of no importance for the other cases. The significance of the experiments with an Al-clay is of course somewhat problematic as Al-ions do not occur as single ions at a pH of 6. Figure I-7 shows that particularly in the case

TABLE I-6. The influence of the order of addition of salt and of methylene blue on the adsorption of methylene blue on montmorillonite at a pH of 6.0

| Clay and salt content | Salt added previously | | Salt added afterwards | |
|---|---|---|---|---|
| | Equilibrium conc. μmole/l | A Units c.e.c. | Equilibrium conc. μmole/l | A Units c.e.c. |
| Na-montm., 0.1 N NaCl | 0 | 0.89 | 0 | 0.89 |
| | 0 | 1.18 | 0 | 1.18 |
| | 20 | 1.69 | 40 | 1.63 |
| Ca-montm., 0.1 N $CaCl_2$ | 0 | 0.89 | 0 | 0.89 |
| | 40 | 1.01 | 40 | 0.99 |
| | 160 | 1.00 | 160 | 0.99 |
| Al-montm., 0.1 N $AlCl_3$ | 10 | 0.84 | 0 | 0.88 |
| | 70 | 0.88 | 40 | 1.02 |
| | 180 | 0.93 | 140 | 1.09 |

FIG. I-6. The adsorption of methylene blue at a pH of 6.0 as a function of the salt concentration and the cationic occupation of montmorillonite

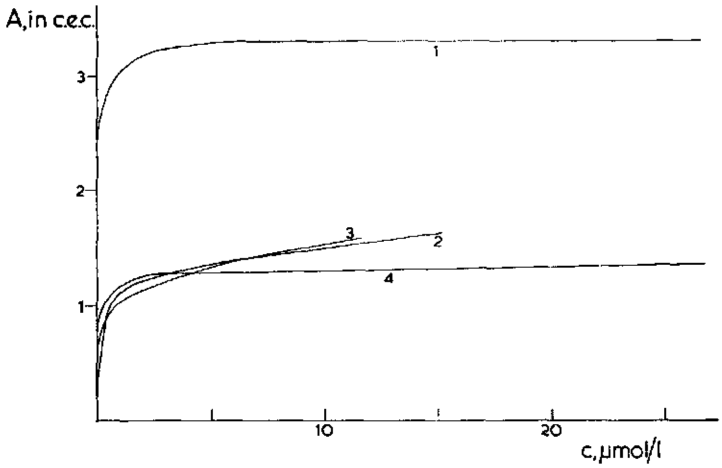


Curve 1: On Na-montmorillonite in 3.6 N NaCl
Curve 2: On Na-montmorillonite in 0.1 N NaCl
Curve 3: On Na-montmorillonite in 0.005 N NaCl
Curve 4: On Ca-montmorillonite in 0.1 N $CaCl_2$
Curve 5: On Ca-montmorillonite in 0.005 N $CaCl_2$
Curve 6: On Al-montmorillonite in 0.1 N $AlCl_3$
Curve 7: On Al-montmorillonite in 0.005 N $AlCl_3$

of kaolinite and montmorillonite the adsorption is strongly preferential in comparison to the inorganic cations Na, Ca or Al. This is not so much the case with illite.

The steepness of the adsorption isotherm explains the so-called irreversibility of methylene blue adsorption as suggested by various authors. Nevertheless repeated

FIG. I-7. The adsorption of methylene blue at a pH of 6.0 for different clay minerals and at different cationic occupation



Curve 1: On Na-kaolinite (Drybranch) in 0.06 N NaCl
Curve 2: On Na-illite (Grundite, L) in 0.005 N NaCl
Curve 3: On Ca-illite (Grundite, L) in 0.005 N $CaCl_2$
Curve 4: On Na-montmorillonite in 0.005 N NaCl

washings with 0.1 N $H_2SO_4$ did lower the amount adsorbed. Thus after 60 portions of 5 litres each, the amount adsorbed on 5 g kaolinite had decreased from 0.86 to 0.22 mmole, corresponding to 3.4 × c.e.c. and 0.88 × c.e.c. respectively. Because of the diminishing rate of desorption the experiment was terminated at this stage, especially since the kaolinite is chemically unstable towards 0.1 N $H_2SO_4$. It could also be shown that adsorbed methylene blue may be removed by certain organic solvents, as e.g. isopropyl alcohol.

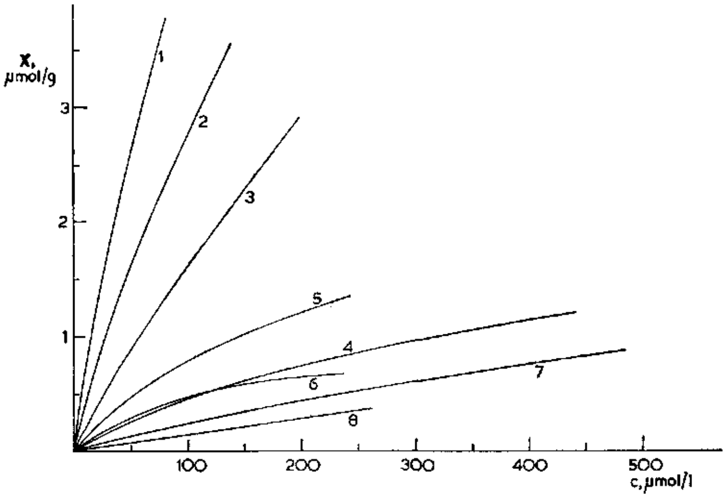
### 4.3.4. *The adsorption of DNC, DNBP, MCPA,* 2,4,5-*T,* 2,4-*D, picric acid and picrolonic acid*

The herbicides DNC, DNBP, MCPA, 2,4,5-T, 2,4-D, picric acid and picrolonic acid are all acids with pK's ranging from 0 to 5. Consequently these compounds may occur either as anion or as undissociated molecules in the pH range of concern for practical applications as herbicides. As was pointed out in section 4.1. anions will be negatively adsorbed on the planar side of the clay minerals, whereas positive adsorption may occur on the edges of the particles. Furthermore the adsorption of undissociated acids should be expected, as well as adsorption due to a salting out effect at very high electrolyte concentrations. Accordingly the pH, the electrolyte concentration and the type of clay mineral were used as variables. In all experiments the adsorption appeared to be fully reversible.

Negative adsorption was particularly evident in the case of montmorillonite at low salt concentrations and high pH values. Also on illite negative adsorption occurred occasionally. A significant adsorption on kaolinite could not be detected under the conditions studied. Positive adsorption was observed at low pH values on all clays. In the figures I-8, -9, -10 the adsorbed quantities are plotted against the equilibrium concentration under various conditions. From the figures it appears that in the concentration range examined the adsorption never reached a saturation value. (The concentration range was limited by the solubility of the compounds). It is also evident that the adsorption may vary with different species of clay minerals, even if belonging to the same type. Thus curve 4 of figure I-8 and curve 1 of figure I-9 differ considerably. It is striking that the slope of the latter curve increases with increasing equilibrium concentration. A similar effect is observed in figure I-10, which gives the adsorption of DNBP and DNC on montmorillonite; the influence of the pH and the species of inorganic cations and anions present is clearly demonstrated.

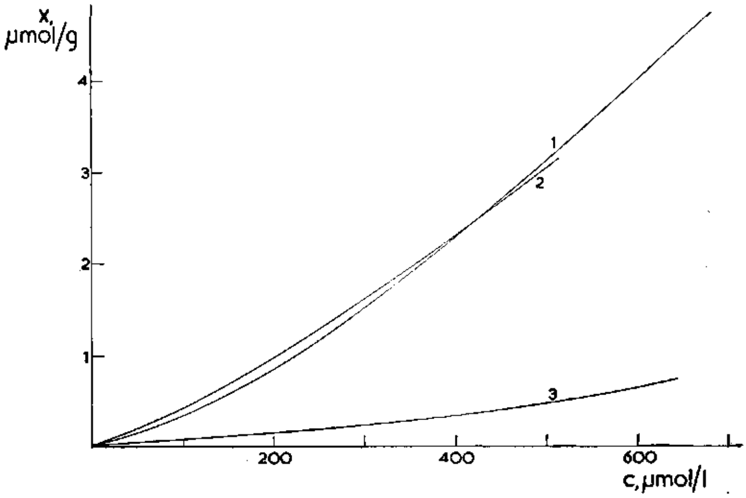
In figures I-11 through -15 the adsorption of the acids studied is given as a function of the pH. The quantity $x_{c=30}$ was again chosen as representative for the adsorption. Negative adsorption occurs in many cases and seems to be independent of the type of organic anion studied. As concerns to montmorillonite it was interesting to note that negative adsorption was apparent even at very low pH values. In the case of illite negative adsorption could only be observed in basic environment. For kaolinite negative adsorption could hardly be detected. In order to limit the number of curves, the negative adsorption for Ca-clays is not shown in the figures mentioned. The positive adsorption is always dependent upon the species of clay and organic compound. On kaolinite little adsorption was found, even at low pH values.

FIG. I-8. Adsorption of different acids on illite (Winsum)



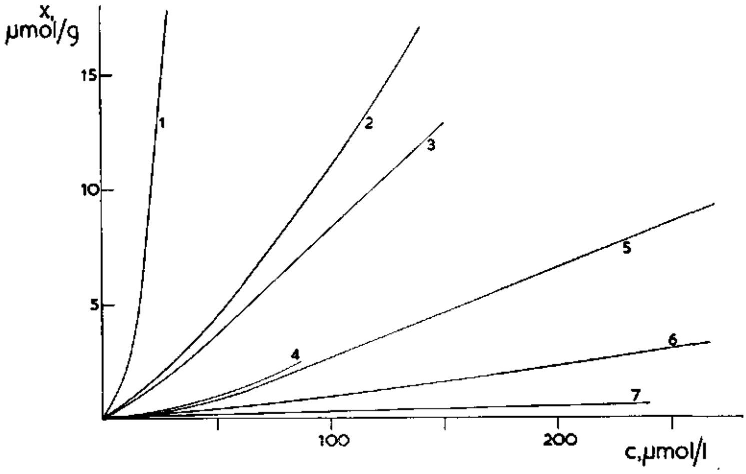
Curve 1: DNC in 0.06 N NaCl, pH 3.4
Curve 2: DNC in 0.01 N NaCl, pH 5.0
Curve 3: 2,4,5-T in 0.06 N NaCl, pH 3.8
Curve 4: 2,4,5-T in 0.06 N NaCl, pH 4.3
Curve 5: Picrolonic acid in 0.04 N NaCl, pH 4.7
Curve 6: Picrolonic acid in 0.04 N NaCl, pH 4.6, also added 0.13 meq. HPAN per g of clay
Curve 7: MCPA in 0.06 N NaCl, pH 4.3
Curve 8: Picric acid in 0.04 N NaCl, pH 4.0

FIG. I-9. The adsorption of different acids on illite (Grundite)



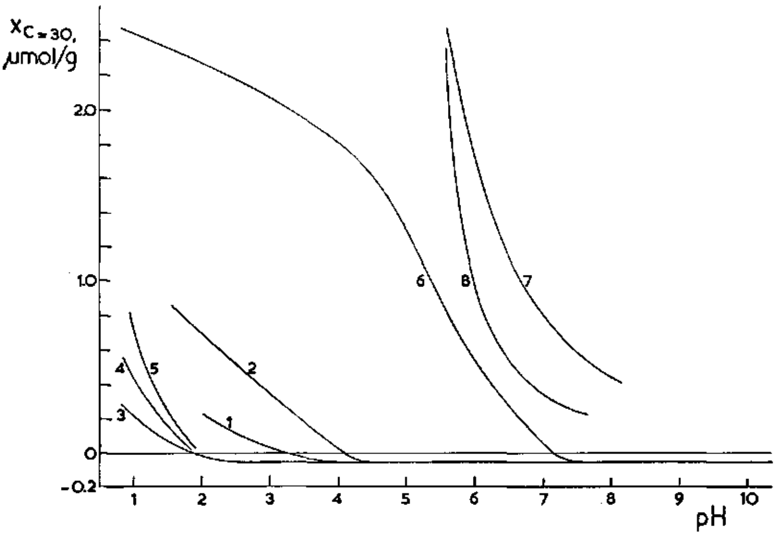
Curve 1: 2,4,5-T in 0.06 N NaCl, pH 4.2 (sample M)
Curve 2: DNBP in 0.02 N CaCl$_2$, pH 6.0 (sample L)
Curve 3: MCPA in 0.06 N NaCl, pH 4.3 (sample M)

FIG. I-10. The adsorption of DNC and DNBP on montmorillonite



Curve 1: DNBP in 3.6 N NaCl, pH 5.0
Curve 2: DNBP in 3.6 N NaCl, pH 5.6
Curve 3: DNBP in 0.06 N NaCl, pH 3.1
Curve 4: DNBP in 3.0 N CaCl$_2$, pH 7.0
Curve 5: DNC in 3.6 N NaCl, pH 7.0
Curve 6: DNC in 3.0 N CaCl$_2$, pH 7.0
Curve 7: DNC in 3.6 N NaClO$_4$, pH 7.0

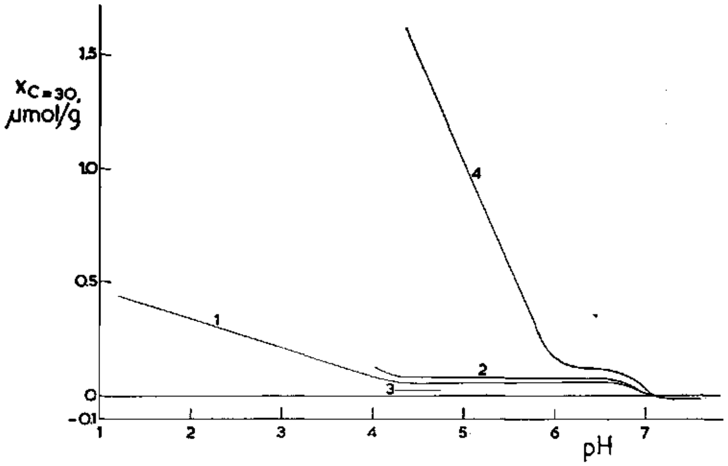
FIG. I-11. The adsorption of different acids on montmorillonite as a function of the pH



Curve 1: 2,4-D in 0.06 N NaCl
Curve 2: 2,4,5-T in 0.06 N NaCl
Curve 3: Picric acid in 0.06 N NaCl
Curve 4: Picric acid in 0.006 N $CaCl_2$

Curve 5: Picric acid in 0.004 N $AlCl_3$
Curve 6: DNBP in 0.06 N NaCl
Curve 7: DNBP in 3.6 N NaCl
Curve 8: DNC in 3.6 N NaCl

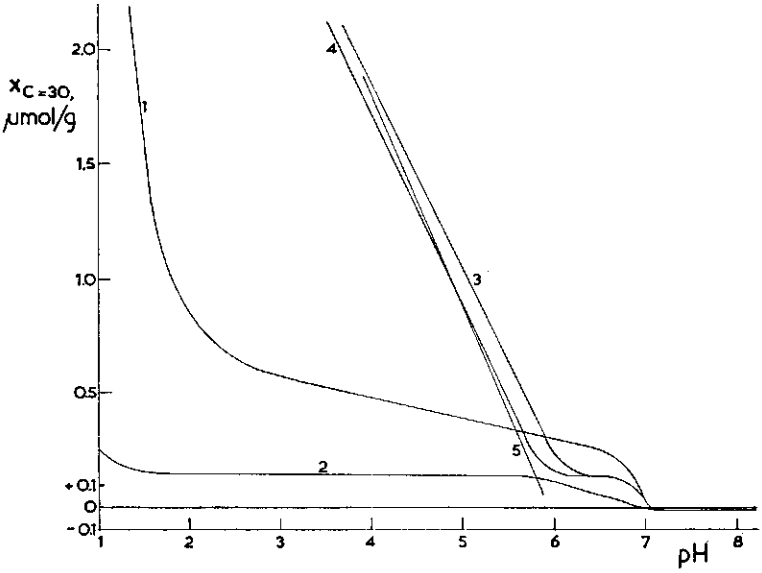
FIG. I-12. The adsorption of different acids on illite (Grundite, M) as a function of the pH



Curve 1: 2,4-D in 0.06 N NaCl
Curve 2: 2,4,5-T in 0.06 N NaCl
Curve 3: MCPA in 0.06 N NaCl
Curve 4: DNBP in 0.06 N $CaCl_2$

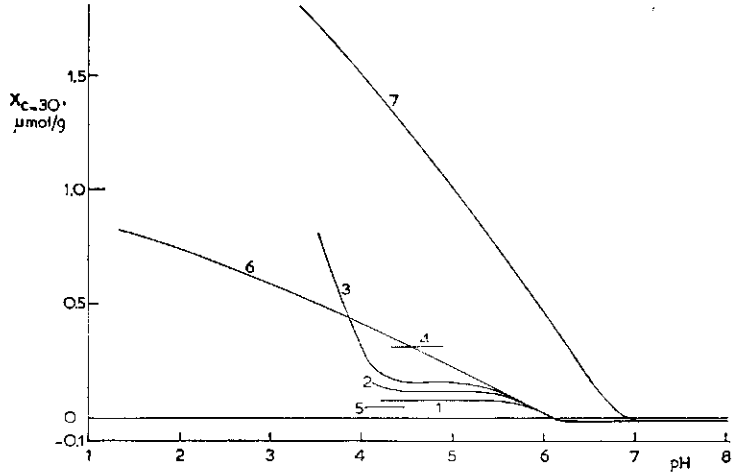
'Curve' 3 is based on the adsorption isotherm of fig. I-9.

FIG. I-13. The adsorption of acids on illite (Grundite, L) as a function of the pH



Curve 1: Picrolonic acid in 0.06 N NaCl
Curve 2: Picric acid in 0.06 N NaCl
Curve 3: DNBP in 0.06 N NaCl
Curve 4: DNBP in 0.06 N $CaCl_2$
Curve 5: DNC in 0.06 N NaCl

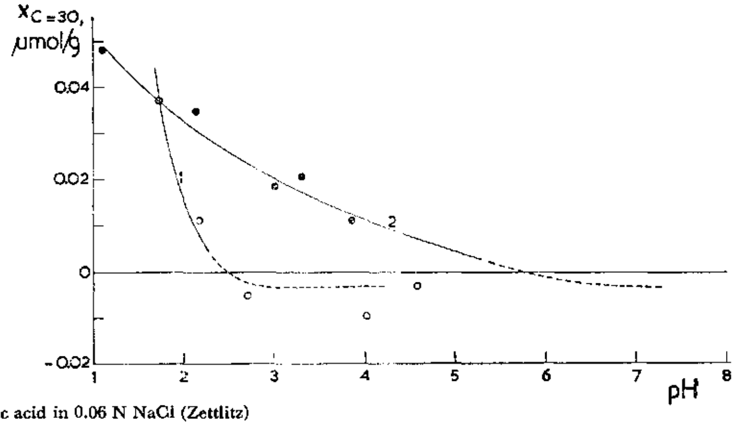
FIG. I-14. The adsorption of different acids on illite (Winsum) as a function of the pH



Curve 1: MCPA in 0.06 N NaCl
Curve 2: 2,4-D in 0.06 N NaCl
Curve 3: 2,4,5-T in 0.06 N NaCl
Curve 4: Picrolonic acid in 0.06 N NaCl
Curve 5: Picric acid in 0.06 N NaCl
Curve 6: DNBP in 0.06 N NaCl and $CaCl_2$
Curve 7: DNC in 0.06 N NaCl

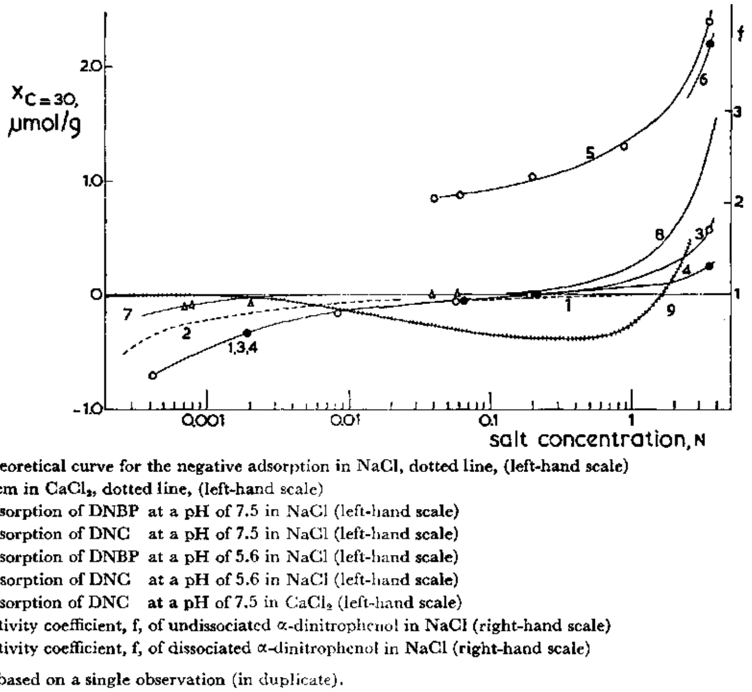
The 'curves' 4 and 5 are based on the adsorption isotherms of fig. I-8.

FIG. I-15. The adsorption of DNBP and picric acid on different kaolinites as a function of the pH



Curve 1: Picric acid in 0.06 N NaCl (Zettlitz)
Curve 2: DNBP in 0.06 N NaCl (Drybranch and Dixieclay)

FIG. I-16. The adsorption of DNC and DNBP on montmorillonite as a function of the salt concentration; as well as the activity coefficients of α-dinitrophenol



Curve 1: Theoretical curve for the negative adsorption in NaCl, dotted line, (left-hand scale)
Curve 2: Idem in $CaCl_2$, dotted line, (left-hand scale)
Curve 3: Adsorption of DNBP at a pH of 7.5 in NaCl (left-hand scale)
Curve 4: Adsorption of DNC at a pH of 7.5 in NaCl (left-hand scale)
Curve 5: Adsorption of DNBP at a pH of 5.6 in NaCl (left-hand scale)
Curve 6: Adsorption of DNC at a pH of 5.6 in NaCl (left-hand scale)
Curve 7: Adsorption of DNC at a pH of 7.5 in $CaCl_2$ (left-hand scale)
Curve 8: Activity coefficient, f, of undissociated α-dinitrophenol in NaCl (right-hand scale)
Curve 9: Activity coefficient, f, of dissociated α-dinitrophenol in NaCl (right-hand scale)
'Curve' 6 is based on a single observation (in duplicate).

The influence of the salt concentration on adsorption is presented in figure I-16. The theoretical curves, both for the negative adsorption on Ca- and on Na-montmorillonite, as well as some calculated curves for activity coefficients which are dealt with in the second part of this publication, are presented. The influence of the type of inorganic anions and cations present in the suspension is demonstrated in figure I-10, curves 5, 6 and 7.

According to the data published by Fripiat (21), Gentili (22), etc. one should expect that the positive adsorption of anions on edges will be highest on kaolinite. This was not borne out by the experimental data. Since Schofield and Samson (52) showed that Cl-ions could be adsorbed by a kaolinite suspension pretreated with dilute HCl, the following treatment was chosen to examine the adsorption of picric acid ions. A 10% Na-kaolinite suspension was shaken with a 2% picric acid solution. After centrifuging and decanting of the clear centrifugate this treatment was repeated seven times, the only anion present now being the picric acid anion. Thereafter the clay was washed with water until the pH of the suspension was 3.9. After raising the pH to 7.9, $6 \times 10^{-3}$ µmole picric acid per g of kaolinite became liberated. Although a faint indication of adsorption of picric acid anions on edges of kaolinite was thus found, the order of magnitude was completely different from the values expected on the basis of Fripiat's measurements (viz. 1 to 4 µmoles per g) (21).

The influence of HPAN-, $PO_4$- and $SO_4$-ions on the positive adsorption of the organic acids studied on illite is presented in figure I-8, curves 5 and 6, and in table I-7. In the tables I-7 and -8 the calculated value for the negative adsorption (cf. Part II, equation 14) is given, the difference between this calculated negative adsorption and the apparent adsorption being the true positive adsorption. The effect of a change in inorganic anions is minor, the polyanion depresses the adsorption of picrolonic acid (and presumably of other anions) considerably.

Table I-7. The influence of the anion on the adsorption of DNBP on illite (Grundite, L) at a pH of 6.0

| Type of salt | Salt conc. normality | $x_{C=30}$, µmole/g | Calculated neg. ads. µmole/g | True pos. ads. µmole/g |
|---|---|---|---|---|
| NaCl | 0.06 | 0.24 | –0.02 | 0.26 |
| NaCl | 0.20 | 0.23 | –0.01 | 0.24 |
| $Na_2SO_4$ | 0.06 | 0.20 | –0.01 | 0.21 |
| $Na_2SO_4$ | 0.20 | 0.20 | –0.00 | 0.20 |
| $CaCl_2$ | $0.36 \times 10^{-3}$ | 0.26 | | |
| $Ca_3(PO_4)_2$ | $0.36 \times 10^{-3}$ | 0.31 | | |

The addition of the 'polyanion' montmorillonite to an illite suspension has no influence on the adsorption of DNC: the quantity adsorbed on a mixture of montmorillonite and illite proved to be equal to the sum of the adsorptions on the single components.

Furthermore a number of observations are of interest. In order to establish whether free aluminum and/or iron hydroxides were of any significance with regard to the adsorption characteristics of the clays studied, a number of experiments was set up using illite (Winsum) pretreated with 0.5 N HCl and with natrium dithionite in acid environment. Although this treatment leads to the removal of both the aluminum and iron hydroxides present, no change in adsorption was observed.

### 4.3.5. *The adsorption of $I^{131}$- and Cl-ions*

As was shown in 4.3.4. the adsorption of organic anions on illite was much larger than the adsorption on kaolinite. As this was contrary to the expectations a number of experiments were executed with $I^{131}$- and Cl-ions to determine the total amount of exchangeably adsorbed anions. For this purpose both a kaolinite (Zettlitz) and an illite (Grundite, L) were treated with NaI in such a manner that the ions present were only Na- and I-ions at a concentration of about $10^{-3}$ N. Subsequently the adsorption of I-ions was determined as a function of the pH and the salt content. In these experiments $I^{131}$ was added as a tracer. The activity of the $I^{131}$-ions was determined with help of a scintillation counter. Comparable experiments were done with Cl-ions, the concentration of which was determined by potentiometric titration with $AgNO_3$, using a silver-silver-chloride electrode as indicator. The experimental results are given in table I-8.

TABLE I-8. Adsorption of Cl- and I-ions on Na-kaolinite and Na-illite

| Type of clay mineral | Type of anion | Salt conc., normality | Apparent adsorption μmole/g | Calculated neg. ads. μmole/g | True pos. ads. μmole/g | pH |
|---|---|---|---|---|---|---|
| Kaolinite (Zettlitz) | $I^{131}$ | 0.006 | − 1.5 | − 1.9 | 0.4 | 6.8 |
| ,, | $I^{131}$ | 0.006 | 0.3 | − 1.9 | 2.2 | 4.3 |
| ,, | $I^{131}$ | 0.006 | 1.5 | − 1.9 | 3.4 | 3.9 |
| ,, | Cl | 0.06 | 0 | − 6.0 | 6.0 | 4.0 |
| Illite (Grundite, L) | $I^{131}$ | 0.06 | − 9 | −30.0 | 21 | 8.0 |
| ,, | $I^{131}$ | 0.06 | 63 | −30.0 | 93 | 4.0 |
| Illite (Winsum) | Cl | 0.01 | −10 | −12 | 2 | 8.5 |
| ,, | Cl | 0.10 | −28 | −38 | 10 | 8.8 |
| ,, | Cl | 0.01 | − 9 | −12 | 3 | 4.5 |
| ,, | Cl | 0.10 | −18 | −38 | 20 | 3.0 |

In addition some experiments were executed to determine the adsorbed quantity of I-ions directly. For this purpose a HI solution (traced with $I^{131}$-ions) of pH 2 was added to the clay suspension. After removal of the excess of I-ions by repeated washings and decantations, the pH was increased in order to establish whether $I^{131}$ was liberated following the increase in pH. After several decantations it was obvious, however, that although the pH was still below 4, practically all I-ions had been removed from the suspension. The adsorption of I-ions on illite and kaolinite is apparently rather non-specific, as the I-ions are replaced by OH-ions at a pH of 4 (cf. Part II).

In all experiments employing iodine extreme care was taken to remove traces of iron in order to avoid any catalytic oxidation of the I-ions.

# PART II. THEORETICAL DISCUSSION

## 1. MECHANISMS OF THE ADSORPTION OF ORGANIC COMPOUNDS ON CLAY MINERALS

### 1.1. ADSORPTION FORCES

Adsorption of solutes at the interface between a solid and a liquid phase will take place if this adsorption, at constant pressure and temperature, leads to a lowering of the Gibbs free energy of the system. When expressing the adsorption in terms of the volume concentration of the adsorbate, present in a layer of finite thickness, one finds that for moderate levels of adsorption the equilibrium situation may be described with the Boltzmann relationship: $n = n_e \cdot \exp(-E/RT)$. In this equation E is the amount of energy liberated when transferring reversibly the adsorbate from the location where the concentration equals $n_e$ to a location where the concentration equals n, expressed per mole of adsorbate. The equilibrium concentration of the adsorbate, $n_e$, is defined at a location outside the range of interaction between adsorbate and interface. Only at low degrees of adsorption (i.e. the adsorption is limited to a single layer and far from a complete monolayer) this adsorption energy may be constant. In other cases (e.g. adsorption in a diffuse layer) the adsorption energy is usually a variable.

The energy of adsorption may be regarded as the total sum of the effects of the different force fields acting between the adsorbent and adsorbate. These forces comprise the Coulomb forces, the Van Der Waals forces (orientation-, induction- and dispersion-forces) and the Born repulsion forces.

In the case of adsorption of solutes on a solid interface from aqueous solutions, it is convenient to distinguish between two types of adsorption, viz. the long range adsorption and the short range adsorption. In the first case adsorption takes place without a significant change of the interaction both between solvent and adsorbent and between solvent and adsorbate. In this case dehydration is not considered and it is assumed that one or more layers of water molecules remain present between adsorbent and adsorbate. The short range adsorption then involves a change of the solvent-adsorbate and the solvent-adsorbent interactions. In the typical case of short range adsorption no solvent molecules will be present between adsorbent and adsorbate.

The long range adsorption, as defined above, is thus concerned only with those forces between adsorbent and adsorbate which have a considerable range of penetration. In the case of clay minerals such forces are the dispersion forces and the forces caused by the interaction between adsorbate and the static electric field emanating from the charged solid interface.

As was mentioned in Part I, section 2, clay minerals consist of platelets of colloidal dimensions, with a length and breadth of about 10 to 1000 times the thickness of the plates. The clay plates are negatively charged because of isomorphous substitution, whereas proton adsorption may lead to the presence of positive charges on the edges. With exception of the regions close to the edges a strong electrostatic field is present around the clay particles, which leads to Coulomb interaction between ions and clay particles. The energy of adsorption, $E_c$, is for this case equal to $ze\psi$, in which ze is the charge of the ion and $\psi$ signifies the potential difference between the region where adsorption takes place and the equilibrium solution.

BUTLER (11) points out that when a polarizable material is displaced in an inhomogeneous electric field the energy is changed. The energy change accompanying the transfer of a volume dV of a polarizable material from a place where the field strength equals zero to a position where it equals F is then found as $\frac{1}{2}\alpha_A F^2 dV$, in which $\alpha_A$ signifies the polarizability of the material per unit volume. Since at the same time an equal volume of solvent is displaced in opposite direction (polarizability $\alpha_B$) the net energy accompanying the transfer equals:

$$E_\alpha = \tfrac{1}{2}(\alpha_A - \alpha_B) F^2 dV \qquad [1]$$

In addition to this effect there will be interaction between the static electric field and particles with a permanent dipole moment. The energy change accompanying the transfer of a particle due to this interaction is:

$$E_p = (p_A - p_B) F dV \qquad [2]$$

where p equals the polarization per unit volume ($p_A$ for the adsorbate, $p_B$ for the solute). p must be defined in such a manner that any change in orientation of the particles is taken into account. If such a change in orientation of the particles is accompanied by a change in entropy of the system, equation [2] is not correct. The equations [1] and [2] do not take into account the fact that the electric field may be influenced by the presence of the adsorbate. Assuming that the adsorbate particles with their hydration shell may be approximated by a spherical particle of considerable size and a mean value of a dielectric constant, BOLT (4) attempted to apply BÖTTCHER'S theory to this case. This leads to the equation:

$$E_\alpha + E_p = {}^1/_6\, a^3 (\varepsilon_A - \varepsilon_B) \frac{3\varepsilon_B}{2\varepsilon_B + \varepsilon_A} F_0^2 \qquad [3]$$

In this equation $a$ equals the radius of the adsorbed particles, $\varepsilon_A$ is the mean value of the dielectric constant of the particle, $\varepsilon_B$ is the dielectric constant of the solvent and $F_0$ equals the field strength which would prevail if the volume of the adsorbate particles is negligible.

Making use of the above considerations it is now possible to make an estimate of the adsorption energy caused by the Coulomb interaction and the interaction resulting from dipole moments and polarization effects. In line with the above reasoning it will be assumed that the interaction between clay and solvent and of the adsorbate with the solvent will remain unchanged if both, the clay and the adsorbate surfaces, are covered with a water layer of at least one molecule thick. These two layers of water will give a distance of at least 4.2 Å. As an example a montmorillonite, saturated with a monovalent organic cation in equilibrium with a 0.01 N solution of a salt of this cation, is chosen. Furthermore the volume, shape, dielectric constant, etc. of the organic adsorbate will be taken equal to those of the known values pertaining to the toluene molecule. In order to calculate the minimum distance for the defined long range adsorption, it will be assumed that the organic ions are situated parallel to the clay surface; the distance between the centre of the ion and the clay surface will then amount to 4.8 Å (the thickness of toluene is about 3.2 Å). As it could be shown by BOLT (3, 4) that the Gouy theory in its simplest form provides a fair description of the behavior of simple inorganic ions in the neighborhood of the clay surface, this theory was used to calculate the adsorption energy. One thus finds that at distances of 5.8 Å and 36 Å resp., the values of $e\psi$ are 6.05 kT and 3.24 kT, resp. This corresponds to 3500 and 1870 cal per gram ion. If furthermore it is assumed that the dielectric constants of water and the adsorbate are 80.4 and 2.4 resp., one finds for the sum of $E_\alpha + E_p$ : 0.031 kT and 0.002 kT (corresponding to 18 and 1 cal per gram ion).

The energy of adsorption due to dispersion forces, $E_d$, may be estimated with help of the equation given by VERWEY and OVERBEEK (57). For the interaction between an adsorbed particle and a planar surface it is found that:

$$E_d = \frac{\pi q \lambda}{6} \left\{ \frac{1}{R^3} - \frac{1}{(R + \delta')^3} \right\} \qquad [4]$$

In this equation q equals the total number of ions ($O^{2-}$, $OH^-$, $Si^{4+}$, $Al^{3+}$, $Mg^{2+}$, etc.) per cm³ of the clay crystal, R equals the distance of the centre of the adsorbed particle to the clay surface and $\delta'$ is the thickness of the clay crystal. $\lambda$ is then equal to $^3/_4\, \alpha_1\, \alpha_2 \cdot \frac{1}{2}(I_1 + I_2)$, in which $\alpha_1$ is the algebraic mean polarizability of the clay ions, $\alpha_2$ the polarizability of the adsorbed particle, $I_1$ is the mean ionisation potential of the clay ions and $I_2$ the ionisation potential of the adsorbed particle. By taking the dimensions of the unit cell of montmorillonite equal to the mean values of those of talcum and pyrophyllite (55) a fair estimate for q may be obtained. Taking now q equal to $18.5 \times 10^{21}$ ions per cm³, $\alpha_{clay}$ equal to 1.75 Å³, $\alpha_{water}$ equal to 1.43 Å³, $\alpha_{toluene}$ equal to 11.57 Å³, $I_{clay}$ equal to 11.02 eV, $I_{water}$ equal to 12.56 eV, $I_{toluene}$ equal to 8.5 eV and $\delta'$ equal to 9.0 Å, it is found that the energy of attraction per mole of toluene situated at a distance of 5.8 Å equals 155 cal per mole and at 36 Å equals 0.35 cal per mole. For water molecules at equal distances one finds 24 and 0.05 cal per mole, resp. By taking into account the density and molecular weights of water and toluene it may be shown that the volume of one mole of toluene equals the volume of 5.89 moles of water. It follows from this that the net energy of adsorption, due to dispersion forces, for toluene from aqueous solutions, situated at a distance of 5.8 and 36 Å resp., amounts to 17 and 0.04 cal per mole of toluene respectively. In this calculation it has not been taken into account that the energy of adsorption will be somewhat less because the medium for which the dispersion forces were calculated is in reality water, whereas calculations were performed for vacuum.

From the above calculation it is obvious that the adsorption of ions in the electric field of a clay mineral is dominated by Coulomb forces.

For short range adsorption the situation is entirely different, in this case all forms of Van Der Waals forces must be taken into account, particularly those with a very small range of penetration. A quantitative treatment of this case is very difficult because the different constants and other essential data are not available. This is evident from the fact that the short range adsorption deals with a situation in which adsorption of the organic material is always accompanied by desorption of water from clay surface and organic material. Thus one has to take into account the net change in Gibbs free energy of the system clay : water and water : organic matter on one hand, compared with the system clay : organic matter and water : water on the other hand. In principle this is also the case for the long range adsorption, but as discussed above this mechanism gives only a small contribution anyway. In addition the interactions with other dissolved components will play a rôle. In certain cases this interaction is roughly known (activity corrections). The Van Der Waals forces can be divided into orientation-, induction- and dispersion-forces. According to DE BOER (2) the orientation effect will only play a significant rôle when the adsorbed particle contains a dipole of considerable dimensions which is situated in such a manner that a close approach to the adsorbent surface is possible. This may be the case for several organic components as e.g. acids and hydroxyl compounds. Since water has, however, also a large dipole moment it may be expected that the adsorption of organic components as a result of orientation should usually be rather small.

An exception may be formed by the H-bonds; this bond is also caused by orientation forces. As the edges of most clay minerals contain OH-groups, as does the basal plane of kaolinite, the formation of H-bonds will have to be taken into account. As an example of this mechanism ILER (32) mentions that organic electron donor compounds may form a complex with SiOH-groups of polysilicic acid. This complex was observed in acidic environment only.

The adsorption energy due to the presence of induction forces is even in the case of short range adsorption small and will not be considered.

In this case the dispersion forces may be of great importance. Since these forces are additive the interaction between all atoms of the adsorbent and adsorbate must be taken into account. As a result all polyatomic molecules will tend to be spread out on the adsorbing surface. Thus aromatic molecules with a flat configuration, likewise those with double bonds and especially conjugated double bonds may be adsorbed rather strongly. Although also aliphatic compounds may accept a planar structure, however, the accompanying loss in entropy will usually outweigh the gain in energy.

## 1.2. ADSORPTION ISOTHERMS

When describing adsorption phenomena one should distinguish between long range and short range adsorption. In the first case, which is of special importance for ions, the order of magnitude of the adsorption energy is comparable to kT. This then results in a diffuse distribution of the ions, in which the adsorption energy is position dependent. This type of adsorption may be treated quantitatively, in the simplest cases with help of the Gouy theory of the diffuse double layer. In case the ions are also subject to short range forces at least a correction must be applied to the Gouy theory treatment.

If the short range forces become dominant in magnitude the adsorbed particles will be concentrated in the immediate environment of the adsorbing surface. In this case the adsorption energy may be considered as a constant for all adsorbed particles. As this adsorption energy is usually not subject to calculation its value must be introduced as a parameter to describe adsorption isotherms, e.g. with the BET or Langmuir theory.

As mentioned above the long range adsorption of ions on charged surfaces, in this case the basal planes of clay minerals, may be described in first approximation with the Gouy theory. Although the requirements that the surface charge should be smeared out homogeneously, that the ions behave ideally and that edge effects may be neglected, are not fulfilled in case of clay minerals, it could be shown by BOLT (5) that the necessary corrections are usually of minor importance. Since the calculations, pertaining to clay systems as they appear in the literature, were usually based on SCHOFIELD's work (51) the notation of the latter author will be approximately followed. SCHOFIELD introduced a new distance parameter in the Gouy theory, making use of the fact that the surface charge of clay minerals is roughly constant. Thus, if one plots the space charge as a function of the distance, it appears that the distance, between the plane where the extrapolated space charge reaches infinity and the plane where the integrated space charge just equals the surface charge density of the clay, is a simple function of the valence of the counter ions, $z^+$, and the surface charge density of the clay. The magnitude of this distance parameter, $\delta$, is then found from:

$$\delta = \frac{4}{z^+ \beta \sigma} \qquad [5]$$

in which $\beta = 8 \pi F^2/1000 \varepsilon RT$; $\varepsilon$ is the dielectric constant, F is the faraday and the other symbols have their usual meaning. The symbol $\sigma$ gives the surface charge density expressed in meq. per cm$^2$; this unit is chosen in order to make the surface charge density more easily comparable to the amount adsorbed. Equation [5] is valid if $\delta << \frac{1}{\varkappa}$ with $\varkappa^2 = \beta I$; I is the ionic strength of the equilibrium solution.

If one now introduces the distance parameter $X = x + \delta$ (in which x equals the distance to the colloid surface) the equations of the double layer theory are conveniently generalized for all systems with a given surface charge density. Defining $u = c^+/c_e^+$ (relative concentration of monovalent cations), one finds for systems containing one type of symmetric salt:

$$u^z = \frac{\cosh \varkappa X + 1}{\cosh \varkappa X - 1} \qquad [6]$$

and for systems containing an asymmetric salt of the 2:1 type (e.g. $CaCl_2$, not $Na_2SO_4$):

$$u^z = \frac{\cosh (\varkappa X + \operatorname{arg\,cosh} 2) + 1}{\cosh (\varkappa X + \operatorname{arg\,cosh} 2) - 2} \qquad [7]$$

(cf. ref. 3). Equations for u may also be derived for systems containing other types of salts or even mixtures of salts. Furthermore one may show that the concentration of ions close to the colloid surface is found from:

$$\Sigma \, (c_s - c_e) = \frac{\beta \sigma^2}{4} \qquad [8]$$

in which $c_s$ and $c_e$ refer to the concentrations, expressed in moles per l, at the colloid surface and in the equilibrium solution respectively. The summation must be extended over all types of ions present in the system. It thus follows that the surface concentrations in systems containing a low or moderate amount of electrolyte depend solely on the type of clay mineral. Substitution of numerical values for montmorillonite indicates that under these circumstances the surface concentration is about 2.6 molar.

Obviously the surface concentration does not specify the total amounts of ions adsorbed. These amounts may be found by an integration of $u^z$ over the entire liquid layer. Thus the amount of monovalent cations adsorbed per cm², $\Gamma^+$, is found from:

$$\Gamma^+ = c_e{}^+ \int_{\delta}^{D} (u^{z^+} - 1) \, dX \qquad [9]$$

in which D is the thickness of the liquid layer, which can be found by dividing the total volume of the liquid by the total surface area. For systems containing a mixture of monovalent ions, it follows that the ratio of the amounts adsorbed equals the ratio of the concentrations in the equilibrium solution, provided no specific attraction forces are taken into account. Departing from a similar assumption **Eriksson** (18) derived an equation for the amount of monovalent cations adsorbed in a system containing a mixture of monovalent and divalent cations (concentration $c^+$ and $c^{++}$ moles per l, resp.). According to **Eriksson**'s equations:

$$\Gamma^+ = \frac{c_e{}^+}{\sqrt{c_e{}^{++}}} \cdot \frac{1}{\sqrt{\beta}} \operatorname{arg\,sinh} \frac{\sqrt{c_e{}^{++} \beta \sigma^2}}{c_e{}^+ + 4 c_e{}^{++}} \qquad [10]$$

For small values of the expression behind the inverse hyperbolic, equation [10] may be simplified to:

$$\Gamma^+ = \frac{c_e{}^+}{c_e{}^+ + 4 c_e{}^{++}} \cdot \sigma \qquad [11]$$

As was shown by **Bolt** (4) equation [10] can also be simplified to equation [12] provided the percentage monovalent ions adsorbed does not exceed 60%. In this equation $\sigma$ is given in meq. per cm², the concentrations are given in moles per l and $\Gamma^{++}$ is the adsorbed amount of divalent ions, in meq. per cm², on the clay surface.

$$\frac{\Gamma^+}{\Gamma^{++}} = \frac{1.4 \times 10^{-7}}{\sigma} \cdot \frac{c_e{}^+}{\sqrt{c_e{}^{++}}} \qquad [12]$$

The Coulomb interaction between a negatively charged clay surface and anions leads to a negative adsorption of these ions. The amount of anions adsorbed negatively, $\Gamma^-$, is found from:

$$\Gamma^- = c_e{}^- \int_{\delta}^{D} (1 - u^{z^-}) \, dX \qquad [13]$$

**Schofield** (51) carried out this integration and derived an equation equivalent to:

$$\Gamma^- = z^- c_e^- \left(\frac{q}{\varkappa} - \delta\right) \qquad [14]$$

In this equation q is a constant which depends on the ratio of the valence of the dominant cation and anion in the system, $z^+/z^-$. One thus finds for $z^+/z^- = 2$, $q = 3 - \sqrt{3}$, for $z^+/z^- = 1$, $q = 2$ and for $z^+/z^- = \frac{1}{2}$, $q = 3$. If the clay suspension is so concentrated that interpenetration of double layers occurs, corrections must be applied to the given equations. For a system containing Na-montmorillonite one may calculate, using the equations given by BOLT and WARKENTIN (7), that the deviations are smaller than 5% as long as the value of $\varkappa D$ is equal to or larger than 3.

For the short range adsorption of ions, in which case in addition to Coulomb forces also the dipole, polarization and dispersion forces mentioned are of concern, the Gouy theory is no longer applicable as such. In certain cases a combination of the Gouy and Stern theories may lead to a reasonable approximation of the situation. Thus GRAHAME (23) distinguishes two groups of ions in the double layer: hydrated and dehydrated ions. The locus of the centres of the dehydrated ions in the first layer is given the name 'inner Helmholtz plane', whereas the plane through the first layer of hydrated ions is named the 'outer Helmholtz plane'. The Gouy theory may now be applied to the ions present in or outside the outer Helmholtz plane. The adsorption of the ions inside the outer Helmholtz plane is then described by means of a Stern equation.

It must be kept in mind, however, that if it is attempted to compute the amount of ions adsorbed under the influence of specific adsorption forces, only those ions present in the immediate neighborhood of the colloid surface are influenced, because of the short range character of these specific forces.

It is now assumed that within the outer Helmholtz plane a single layer of ions, (e.g. g-ions) is adsorbed, subject to an extra adsorption energy, $\varphi_g$, in addition to the Coulombic forces.

Furthermore it is assumed that the thickness of this layer is equal to 2r and that the charge of these ions is located in a plane at a distance r from the colloid surface. The potential in this plane is $\psi_r$. Because of crowding effects in this first layer one also has to introduce a factor, b, correcting the number of available positions. One then finds:

$$\frac{g_s}{g_e} = \frac{b_s}{b_e} \cdot \exp\{(-ze\psi_r - \varphi_g) / kT\} \qquad [15]$$

It is found, however, that for montmorillonite the available surface area per ion equals 140 Å$^2$ and unless the adsorbed ion is very large in size or $\varphi_g$ is large in comparison to $ze\psi_r$, both $b_s$ and $b_e$ may be taken equal to unity. In the case of organic ions of larger size and also in the case of illites and kaolinites the crowding factor may not be neglected.

The calculation of the amount adsorbed from $g_s$ usually involves the knowledge of the thickness of the adsorbed layer. If it is assumed, that $\varphi_g$ is so small that $\psi_r$ is hardly changed in comparison to the case in which $\varphi_g = 0$ and that $\varphi_g$ is the same for ions and uncharged molecules one may avoid the estimate of the thickness of the adsorbed layer, provided the relationship between the absorbed amount of uncharged molecules and their equilibrium concentration, f(g) is known. If one now calculates, with help of double layer theories, the accumulation of g-ions on the surface due to Coulombic forces, one may use this surface concentration as the apparent equilibrium concentration. The extra amount of the ions adsorbed in the Stern layer because of the presence of $\varphi_g$, $g_{st}$, is then found from:

$$g_{st} = f(g) \cdot g_s \tag{16}$$

in which $g_s$ is the mentioned apparent equilibrium concentration.

If only $g^+$ and $c^+$ cations are present one may, neglecting the anions close to the surface, introduce:

$$c_s^+ + g_s^+ = \Sigma_s \tag{17}$$

in which $\Sigma_s$ is the total concentration of ions close to the surface. With help of:

$$\frac{g_s^+}{c_s^+} = \frac{g_e^+}{c_e^+} \tag{18}$$

and equation [8] one now finds:

$$g_s^+ = \frac{g_e^+}{g_e^+ + c_e^+}\left(\frac{\beta\sigma^2}{4} + \Sigma_e\right) \tag{19}$$

in which $\Sigma_e$ is the total concentration of ions present in the equilibrium solution. In the presence of $g^{++}$ and $c^+$ ions one finds in the same manner, starting from:

$$\frac{\sqrt{g_s^{++}}}{c_s^+} = \frac{\sqrt{g_e^{++}}}{c_e^+} \tag{20}$$

the equation:

$$g_s^{++} = \Sigma_e + \frac{\beta\sigma^2}{4} - \frac{(c_e^+)^2}{2g_e^{++}}\left\{\sqrt{1 + \frac{g_e^{++}}{(c_e^+)^2}(\beta\sigma^2 + 4\Sigma_e)} - 1\right\} \tag{21}$$

In the presence of $g^{++}$, $g^+$ and $c^+$ ions these equations are:

$$g_s^+ = \frac{g_e^+(c_e^+ + g_e^+)}{2g_e^{++}}\left\{\sqrt{1 + \frac{g_e^{++}}{(c_e^+ + g_e^+)^2}(\beta\sigma^2 + 4\Sigma_e)} - 1\right\} \tag{22}$$

and

$$g_s^{++} = \Sigma_e + \frac{\beta\sigma^2}{4} - \frac{(c_e^+ + g_e^+)^2}{2g_e^{++}}\left\{\sqrt{1 + \frac{g_e^{++}}{(c_e^+ + g_e^+)^2}(\beta\sigma^2 + 4\Sigma_e)} - 1\right\} \tag{23}$$

In those cases where $g_e^{++}$ is small in comparison to $g_e^+ + c_e^+$ the equations [22] and [23] can be simplified to:

$$g_s^+ = \frac{g_e^+}{g_e^+ + c_e^+}\left\{\frac{\beta\sigma^2}{4} + \Sigma_e - \frac{\frac{1}{2}\, g_e^{++}}{8(c_e^+ + g_e^+)^2}(\beta\sigma^2 + 4\Sigma_e)^2\right\} \tag{24}$$

and

$$g_s^{++} = \frac{\frac{1}{2}\, g_e^{++}}{8(c_e^+ + g_e^+)^2}(\beta\sigma^2 + 4\Sigma_e)^2 \tag{25}$$

With increasing magnitude of $\varphi_g$, at a given value of $g_e^+$, the value of $\psi_r$ will decrease, indicating that the Coulombic contribution to the adsorption energy becomes of lesser importance. Obviously the Gouy approach loses all significance if $\psi_r$ becomes very small and for these systems a monolayer type adsorption equation should be a satisfactory approximation.

If $\varphi_g$ is very large, reversal of charge will occur, which may then again lead to the formation of a diffuse layer, in this case containing anions as counter ions. The next layer of ions will now consist mainly of negative ions $c^-$; the charge of this layer of ions is thought to be concentrated in a plane at a distance $2r + d$ from the clay surface. If the electric potential in this plane is taken equal to $\psi_d$, one finds, because no charge is present between the locations r and $2r + d$:

$$\sigma_g^+ - \sigma = \frac{(\psi_r - \psi_d)\varepsilon'}{4\pi(r + d)} \qquad [26]$$

In this equation $\sigma_g^+ - \sigma$ equals the charge of the adsorbed g-ions minus the charge of the clay mineral.

The adsorption of uncharged particles is governed by short range forces only. For the description of this phenomenon one either departs from Langmuir's theory or from the BET theory. The first approach departs from the assumption that the adsorption takes place in a monolayer, whereas the second theory takes into account the formation of several layers. **Brunauer** et al. (10) distinguish between 5 types of adsorption isotherms. Several of these types are based upon the presence of the close proximity of different adsorbing surfaces; these types are of minor concern for clay minerals in aqueous environment. Thus only the types II (S-shaped, concave-convex) and III (convex) are of concern. The adsorption equation pertaining to these cases is:

$$\frac{c/c_0}{x\,(1 - c/c_0)} = \frac{K-1}{x_m K} \cdot \frac{c}{c_0} + \frac{1}{x_m K} \qquad [27]$$

in which $c_0$ is the saturation concentration, $x_m$ is the maximum amount which can be adsorbed in the first layer and K is a constant. K is in first approximation equal to $\exp\,[(E_1 - E_L)/RT]$ in which $E_1$ is the mean molar heat of adsorption for the first layer and $E_L$ is the molar heat of crystallization of the solute under consideration.

If
$$\frac{c/c_0}{x(1 - c/c_0)}$$
is plotted against $c/c_0$, the above equation leads to a straight line; $x_m$ and K, and therefore $E_1 - E_L$ may then be determined from the slope and intercept of the line. The S-shaped curve may be expected if $K \gg 1$, i.e. if the heat of adsorption, $E_1$, is much larger than the heat of crystallization, $E_L$. In the opposite case $E_1 < E_L$ the convex adsorption isotherm will arise. If $E_1$ just equals $E_L$ equation [27] may be simplified to:

$$\frac{c/c_0}{x\,(1 - c/c_0)} = \frac{1}{x_m} \qquad [28]$$

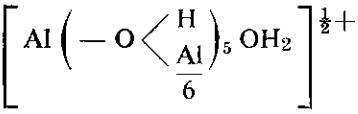
In general the BET equations are valid in a limited range of concentrations. Especially if only a small portion of the surface is occupied, deviations will occur because of selective adsorption on isolated places which invalidate the assumption of a constant value of the adsorption energy.

It should be remembered that agreement between the actual adsorption isotherms and the predicted isotherms from BET theory does not warrant the validity of the assumptions implied, i.c. constancy of the adsorption energy. As could be shown by HALSEY (27) one may derive adsorption curves of similar shape departing from the validity of a distance dependency of the adsorption energy similar to that of the London–Van Der Waals energy, provided an exponential distribution for the adsorption energies of the molecules in the first layer was assumed.

## 1.3. INFLUENCE OF pH AND SALT CONCENTRATION ON THE ADSORPTION

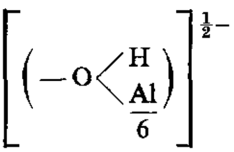
The adsorption of organic compounds on clay minerals is dependent on different factors. Of primary concern is the pH of the system, since both the dissociation of the organic compounds and the charge distribution on the clay minerals are dependent upon the pH. As was mentioned before the lattice of clay plates usually contains a permanent negative charge as a result of isomorphous substitution. The edges contain AlOH- and SiOH-groups which are subject to a proton dissociation/association mechanism. At low pH values these edges may thus attain a positive charge which would lead to the adsorption of anions. Although only few data are available on the positive adsorption of anions by clays, one may conclude from the work of FRIPIAT (21), CASHEN (12), BOLT and WARKENTIN (7) that such a positive adsorption of Cl-ions may be of more importance for kaolinite than for montmorillonite. No definite information is available on the existence of positive edge charges on illite. Especially the pH values at which reversal of charge of the edges would occur are usually not known. It may be attempted to make an estimate of this pH value by a comparison between the OH-groups on clay edges and those on silica and alumina sols. In acid environment the aluminum occurs in the form of $Al(OH_2)_6^{3+}$ ions. According to SCHOFIELD (53) the dissociation reaction of the first proton has a pK value of 5.15. Upon a further increase in pH the second proton will dissociate; presumably this second dissociation is preceded by the beginning of polymerisation. Next further dissociation and polymerisation advance together until at a pH value between 5.5 and 6.5 about 2.5 protons are dissociated per aluminum atom. The dissociation of 3 protons (corresponding to an electrically neutral lattice of $Al(OH)_3$) is found at a pH between 8 and 9. When the pH is increased even further, a negatively charged surface is obtained. Negatively charged AlOH-groups seem of little concern for montmorillonite and illite as compared to the amount of charge derived from the isomorphous substitution. As it is known (SCHUYLENBORGH, 54) that upon crystallization the pK values of surface OH-groups are usually shifted downwards, these data may not be applied to clay lattices without corrections. The zero point of charge of silica sol is found at a pH of about 3 (BOLT, 6). Also in this case a well crystallized lattice will probably exhibit a lower pK value for the dissociation reaction (Quartz exhibits an isoelectric point of 2 or below).

In clays the situation is even more complicated because here the edge Al-atoms are usually bonded to one or more Si-atoms via an O-atom. Departing now from the gibbsite surface as a model for clay edge AlOH-groups one may attempt to apply various corrections for the conditions prevailing. This surface may be described with the formula:



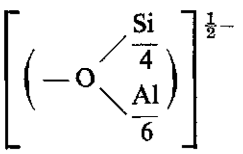
$$\left[\mathrm{Al}\left(-\mathrm{O}\left\langle\begin{matrix}\mathrm{H}\\ \frac{\mathrm{Al}}{6}\end{matrix}\right.\right)_5\mathrm{OH_2}\right]^{\frac{1}{2}+}$$

in which the notation $\frac{\mathrm{Al}}{6}$ is used to indicate that the aluminum atoms are in hexa coordination with the O-atoms. The pH at the zero point of charge thus corresponds to the pK of the dissociation of the first protons of this surface; this pH is situated between 8 and 9. When part of the



$$\left[\left(-\mathrm{O}\left\langle\begin{matrix}\mathrm{H}\\ \frac{\mathrm{Al}}{6}\end{matrix}\right.\right)\right]^{\frac{1}{2}-}$$

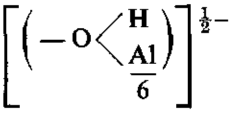
groups are replaced by



$$\left[\left(-\mathrm{O}\left\langle\begin{matrix}\frac{\mathrm{Si}}{4}\\ \frac{\mathrm{Al}}{6}\end{matrix}\right.\right)\right]^{\frac{1}{2}-}$$

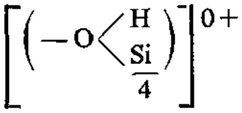
groups

(in which the notation $\frac{\mathrm{Si}}{4}$ is used to indicate that the silicium atoms are in tetra coordination with the O-atoms) as is the case in clay minerals, the pK value of the above mentioned proton should be decreased as a result of the extra repulsion due to the $Si^{4+}$ ion. As a consequence, the edge $AlOH_2$-groups in montmorillonite and illite (2:1 type) should be more acidic than those in kaolinite (1:1 type). In addition to these several other types of $AlOH_2$-groups will occur on the edges of clay particles. Of these, the type in which a



$$\left[\left(-\mathrm{O}\left\langle\begin{matrix}\mathrm{H}\\ \frac{\mathrm{Al}}{6}\end{matrix}\right.\right)\right]^{\frac{1}{2}-}$$

group is replaced by a



$$\left[\left(-\mathrm{O}\left\langle\begin{matrix}\mathrm{H}\\ \frac{\mathrm{Si}}{4}\end{matrix}\right.\right)\right]^{0+}$$

group,

should be more acidic than the one above.

Other possibilities are quantitatively of lesser importance. Thus it may be concluded that the least acidic $OH_2$-group is still more acidic than those in gibbsite. Accordingly positive charge will probably disappear from the edges between, say pH 5 and 7.

Although the reversal of charge of the edges should have a profound influence on the viscosity of clay suspensions, little information could be gained from the literature. Usually the pH was not employed as a variable, and most of the older experiments were conducted on clays prepared from H-clays. As the H-clays are chemically unstable (34, 36) and change over into aluminum clays, these measurements are of little value. A recent publication of NASH (43) gives the viscosity of montmorillonite suspensions as a function of the pH. In acid environment the viscosity is higher than in basic environment and the transition occurs at a pH of about 6.

Aside from the above, the influence of the pH on the adsorbate should be considered.

The pK values of the acids studied vary between 0.40 and 4.40, accordingly these compounds will, in the pH range studied, occur both in dissociated and undissociated form. Thus if the amount adsorbed at a given value of the equilibrium concentration, is plotted as a function of the pH, one should expect both an adsorbent-dependent and an adsorbate-dependent pH effect.

In case of weak bases, e.g. substituted ureïdes and triazines (pK varying between 1.9 and –1 to –2) the adsorption in cationic form will only be of importance at low pH values. In this case it has to be taken into account that the H-ion concentration in the double layer is considerably higher than that in the equilibrium solution; thus the concentration of the positive ions should be corrected for local pH values. Especially in case of systems containing a low concentration of indifferent salts, corresponding to a large difference in electric potential between solution and plate surface, the H-ion concentration will be much higher in the double layer than in the equilibrium solution. This increased association with protons is supported by the work of Delvaux (14) who showed that the H-ions present in the double layer of clay minerals have an influence on the catalytic inversion of sucrose.

Finally the salt concentration will influence the adsorption, due to salting-out effects. In interpreting this effect it should be remembered that a change in electrolyte concentration in the equilibrium solution will hardly influence the situation close to the colloid surface. Therefore increase of electrolyte in solution will usually increase the activity coefficients in solution without notably effecting those near to the colloid surface. This will then lead to an increase of the adsorption.

The influence of electrolyte concentration on the activity coefficients of the adsorbate studied may be estimated by a comparison with chemically related compounds. Thus the data on α-dinitrophenol (Harned and Owen, 28) may be used in order to obtain an estimate for the behavior of DNC and DNBP. In figure I-16 the molar activity coefficient of the undissociated α-dinitrophenol, $f_{HR}$, and the square of the mean ionic molar activity coefficient, $(f_H f_R)^{\frac{1}{2}}$, are given. The mentioned activity coefficients are defined as follows: $a_{HR} = f_{HR} \cdot c_{HR}$ and $a_s = c_s \cdot (f_H f_R)$, in which $a_{HR}$ is the activity of the undissociated acid, $c_{HR}$ is the concentration of the undissociated acid, $c_s$ is the concentration of the dissociated part of the acid and $a_s$ is the activity of the dissociated acid. It follows from figure I-16 that the activity coefficient of both the dissociated and the undissociated acid increases at high salt concentrations. An increase of the electrolyte concentration in solution from $10^{-3}$ to 2 N will thus cause an increase in adsorption.

# 2. THE ADSORPTION OF ORGANIC COMPOUNDS ON THE MERCURY SURFACE

As was shown in section 1 the adsorption of organic compounds on solid/liquid interfaces is determined by a larger number of factors. These factors are only partly known in a quantitative or even in a qualitative sense. As the adsorption on the mercury surface has been studied to a considerable extent it seems logical to investigate whether the observed results are applicable to the adsorption on clay minerals. Obviously the methods used in these investigations are not applicable to clay systems. Thus the investigations of the mercury surface are done by means of the analysis of the electrocapillary curve. For clays neither the surface tension nor the exact value of the surface potential is known and as a result this curve cannot be determined for clay minerals.

In a qualitative sense some of the results obtained from the study of the electrocapillary curve of the mercury may be applied to clays. Thus it was found that in contrast to inorganic cations, anions and organic cations are often adsorbed preferentially (i.e. to a larger extent than should be expected on the basis of Coulomb adsorption). This difference in adsorption is caused mainly by the fact that anions and organic cations are easily dehydrated. It should be expected, therefore, that, due to the unevenness of the edge surface of clay crystals and the important influence of geometric factors on the short range Van Der Waals forces, considerable specific effects for these ions should be expected.

# 3. DISCUSSION OF EXPERIMENTAL DATA

In the following section it will be attempted to interpret the experimental data, presented in Part I of this publication in the light of the given theory. For this interpretation it is necessary to establish which of the mentioned adsorption mechanisms may be of concern. Furthermore it will be checked, if possible, whether the observed adsorption can be explained in a quantitative manner by means of this theory.

## 3.1. THE ADSORPTION OF METHYLENE BLUE

It is obvious from the data presented in Part I (cf. fig. I-6 and -7) that the cations of the strong base methylene blue are adsorbed preferentially in comparison to other cations. In fact the adsorbed amount is often higher than the c.e.c. Furthermore it appears that the adsorption on Na-montmorillonite exceeds that on Ca- and Al-montmorillonite. EMODI (16) suggests that in case of exchange between Ca-ions and methylene blue ions an inclusion of Ca-ions may occur as a result of the size of the methylene blue ions. An estimate of the surface area covered by a methylene blue molecule in a position parallel to the surface, derived from structure models, gives a value of about 102 Å². This is in good agreement with the value derived from the empirical relationship of LIVINGSTON (35):

$$\text{Surface area} = F\left(\frac{M}{N_{av}\rho}\right)^{2/3} \qquad [29]$$

using for the factor F the experimental value as found for benzene. This factor, F, depends on the shape of the molecule and the type of packing; M is the molecular weight and $\rho$ the density. Since the surface area, available per unit charge in montmorillonite, is about 140 Å², inclusion of small cations, as suggested by EMODI, does not seem probable.

One can show that for a complete coverage of montmorillonite with methylene blue ions (using 102 Å² per ion) the total amount stored in a monolayer must be 1470 µmoles per g. Looking at the experimental data of Na-montmorillonite (0.1 N NaCl), it is found that the adsorption curve flattens out at an adsorbed amount of about 1500 µmoles per g; this situation is reached at an equilibrium concentration of about 10 µmoles per l. Under these conditions the Na-montmorillonite thus contains an excess of methylene blue and must exhibit reversal of charge. The net (positive) charge density is then found by subtracting the plate charge from the total charge of the methylene blue ions. Making use of equation [8] one may thus calculate the concentration of Cl-ions in close proximity of the adsorbed layer of methylene blue. From this surface concentration of Cl-ions one may then estimate the surface potential, $\psi_d$. With help of equation [26], the potential in the adsorbed layer of methylene blue, $\psi_r$, may be estimated. Taking the diameter of Cl-ions as 5.1 Å and the thickness of the methylene blue layer as 3.9 Å, one finds $r + d = 4.5$ Å. The value of the dielectric constant in this part of the double layer is taken at about 30. For the calculation of $\varphi_g$ with the Stern equation [15] it is now necessary to make an estimate of the crowding factor $b_s/b_e$. Since at high concentrations $b_s$ approaches zero, this calculation was executed at an equilibrium concentration of 2 μmoles per l. If it is then assumed that the first layer is filled at an equilibrium concentration of 10 μmoles per l, one may put:

$$b_s = \frac{A(10\ \mu\text{moles}) - A(2\ \mu\text{moles})}{A(10\ \mu\text{moles})} \qquad [30]$$

in which A is the amount adsorbed in units c.e.c. For the equilibrium solution $b_e$ may be taken equal to 1. The concentration of methylene blue in the adsorbed layer is now found from $g_s = (A \times \text{c.e.c.}) / (2r \times S)$, in which S is the specific surface area and A × c.e.c. is the adsorbed amount per g of clay. The results of these calculations are given in table II-1. The calculated value of $\varphi_g$ does not seem unreasonable, especially in view of the results of the BET analysis to be discussed in the following section.

TABLE II-1. The adsorption of methylene blue on clay minerals interpreted according to the theory of Stern

| Type of clay mineral | Type of salt | $c_e^-$ Cl-ions normality | $\sigma_g^+ - \sigma$ meq./cm$^2$ ($\times 10^{-7}$) | $c_s^-$ Cl-ions normality | $\psi_d$ mV | $\psi_r$ mV | $b_s$ ($\times 10^{-3}$) | $\varphi_g$ cal/mole ($\times 10^3$) |
|---|---|---|---|---|---|---|---|---|
| Montmorillonite | NaCl | 0.100 | 0.70 | 1.28 | 64 | 177 | 36 | 14.5 |
| ,, | NaCl | 0.005 | 0.27 | 0.189 | 91 | 134 | 82 | 12.8 |
| ,, | $CaCl_2$ | 0.100 | – | – | – | 205 | 62 | 14.5 |
| ,, | $CaCl_2$ | 0.005 | – | – | – | 130 | 47 | 12.8 |
| ,, | $AlCl_3$ | 0.100 | – | – | – | 198 | 49 | 14.5 |
| ,, | $AlCl_3$ | 0.005 | – | – | – | 138 | 61 | 12.8 |
| Illite (Grundite, L) | NaCl | 0.005 | 0.21 | 0.116 | 79 | 133 | 187 | 12.2 |
| ,, | $CaCl_2$ | 0.005 | 0.13 | 0.047 | 56 | 77 | 260 | 10.6 |

For the Ca- and Al-montmorillonite this method cannot be used because now obviously inclusion of cations is present. This conclusion is based on the fact that even those Ca- and Al-montmorillonites which contain an adsorbed amount of methylene blue smaller than the c.e.c., still exhibit positive charge as apparent from electrophoresis measurements. It was argued before that the size of the methylene blue molecules does not suggest an inclusion of cations between the methylene blue and the clay surface; these systems have, however, other characteristics which may lead to a form of inclusion. As will be discussed in section 3.3., it could be shown by various authors that in Ca- and Al-montmorillonite the platelets do not occur singly, but that a condensation of plates to larger units has taken place. It is quite probable that the strongly adsorbed methylene blue ions penetrate between the plates of the montmorillonite polyplates without allowing the original ions to be completely replaced. It is interesting to note that in case of illite, where probably these units with internal exchange surfaces are not formed, little difference was observed between the 'saturation' values of methylene blue. Although thus the calculations as given for Na-montmorillonite cannot be executed for Ca- and Al-montmorillonite, one may still attempt to back-calculate $\psi_r$ for the Ca- and Al-montmorillonite, assuming that the value of $\varphi_g$ is of about the same magnitude for Na-, Ca- and Al-montmorillonite at the same normality of the Na-, Ca- and Al-ions, respectively. These estimates are included in table II-1.

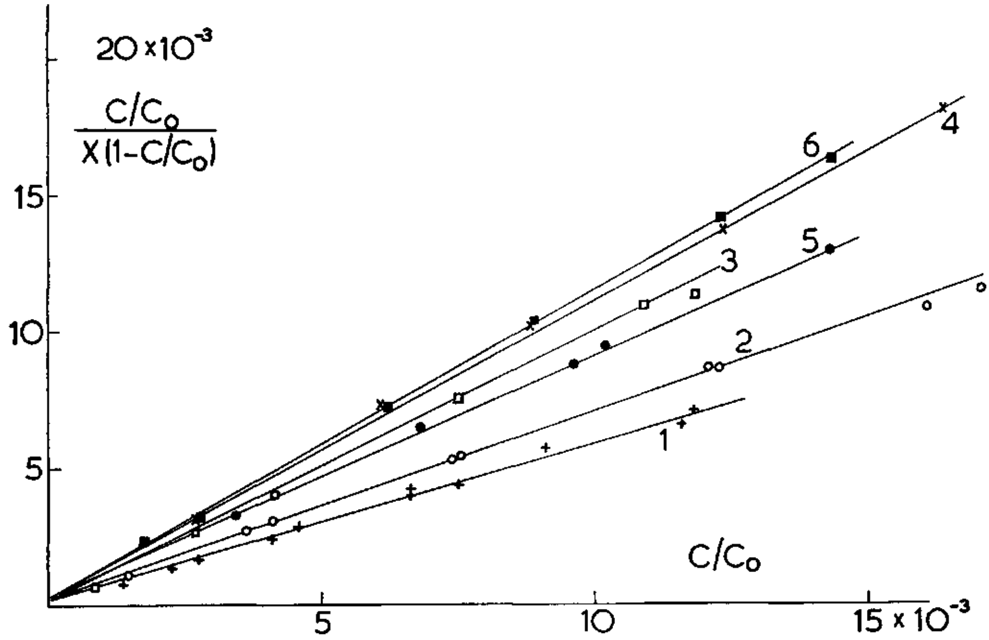
Aside from differences in adsorption energy the shape of the adsorption curve is also of interest. Thus the adsorption curves for the montmorillonites exhibit a rather sudden transition in slope when reaching the saturation plateau, whereas those for the illites have a much more gradual character. This may be the explanation of the differences between Fairbairn and Robertson (20) on one hand and Peter and Markert (46) on the other hand. The first authors probably used montmorillonites whereas Peter et al. were studying soil clays of Western Germany which are generally illitic in nature. The fact that the 'saturation' plateau is much better defined for montmorillonites could be the reason that Fairbairn et al. developed a method for the determination of the c.e.c. based on the adsorption of methylene blue (cf. Part I, section 3.3.2.).

For Na-kaolinite the 'saturation' value is reached when the surface area covered by one molecule equals 40 Å$^2$. Since the surface area of the methylene blue molecule in planar position was taken equal to 102 Å$^2$, the adsorption apparently does not take place in the form of a monolayer of molecules in planar position. Accordingly the relationships above cannot be used to describe this system. The different behavior of kaolinite may be caused by the presence of OH-groups on one of the planar sides of the crystal (montmorillonite and illite do not carry OH-groups on the planar sides).

The values of the adsorption energies calculated above indicate that the adsorption is governed to a large extent by non-Coulombic forces. Accordingly the adsorption may possibly be described by means of BET isotherms. In figure II-1 the data of Part I are plotted according to the method of Brunauer et al. In the range of $c/c_0$ between 0.002 and 0.015 all points lie on a straight line. Although Brunauer et al. state that their theory is applicable in the range 0.05 to 0.35, it is conceivable that, because of the high surface coverage with methylene blue in the range observed, application of the BET theory is possible. In table II-2 the degree of surface coverage for a complete monolayer and the difference between heat of adsorption and heat of crystallization, $E_l – E_L$, as calculated according to BET, are given. These calculated values of surface coverage are usually higher than those found at an equilibrium concentration of 10 $\mu$moles per l. Nevertheless the agreement seems satisfactory, especially in view of the fact that in the BET theory a varying Coulombic contribution to the adsorption energy is not taken into account. The calculated values of the difference between energy of adsorption and energy of crystallization would indicate that the adsorption energy as found from the Stern theory is only about twice this amount.

Summarizing it would seem warranted to conclude that, notwithstanding the approximate character of the calculation described, methylene blue is adsorbed by

FIG. II-1. The adsorption of methylene blue on different montmorillonites, plotted according to the BET method



Curve 1: Na-montmorillonite, 0.1 N NaCl
Curve 2: Na-montmorillonite, 0.005 N NaCl
Curve 3: Ca-montmorillonite, 0.1 N $CaCl_2$
Curve 4: Ca-montmorillonite, 0.005 N $CaCl_2$
Curve 5: Al-montmorillonite, 0.1 N $AlCl_3$
Curve 6: Al-montmorillonite, 0.005 N $AlCl_3$

TABLE II-2. The adsorption of methylene blue on clay minerals interpreted according to the BET theory

| Type of salt | Salt, normality | A, monolayer, according to BET | A at $g_e$ = 10 μmoles per l | Surface area per molecule adsorbed in Å² | $E_1 - E_L$ cal/mole (× $10^3$) |
|---|---|---|---|---|---|
| NaCl | 0.100 | 1.70 | 1.60 | 82 | 5.0 |
| NaCl | 0.005 | 1.43 | 1.23 | 98 | 4.7 |
| $CaCl_2$ | 0.100 | 1.00 | 0.91 | 140 | 5.3 |
| $CaCl_3$ | 0.005 | 0.91 | 0.82 | 154 | 5.0 |
| $AlCl_3$ | 0.100 | 1.10 | 0.97 | 127 | 4.9 |
| $AlCl_3$ | 0.005 | 0.88 | 0.77 | 159 | 4.8 |

means of specific forces leading to an energy of adsorption of about 10 to 15 kcal per mole. It was established that the adsorption takes place roughly as a monolayer, indicating that the binding forces between clay and methylene blue are considerably larger than the forces between subsequent layers of methylene blue. The observed reversal of charge in case of Ca- and Al-montmorillonite must be due to inclusion of inorganic cations, probably between the individual platelets of the composite clay particles. It would be of interest to investigate whether the rate and amount of exchange, when preparing a Na-montmorillonite from a Ca-montmorillonite covered with methylene blue is substantially less than that for a pure Ca-montmorillonite.

### 3.2. THE ADSORPTION OF SUBSTITUTED UREÏDES AND TRIAZINES

The weak bases CMU and DCMU (pK -1 to -2) and the bases simazine, chlorazine and trietazine ($pK_1$ 1.4 to 1.9, $pK_2$ about 0) may be adsorbed both as neutral molecules and as positively charged ions. In neutral and basic environment the influence of Coulomb forces may be neglected. For $c/c_0$ values up to 0.25 the adsorption isotherms, in this pH range, are linear in several cases (cf. fig. I-1, curves 2 and 3; fig. I-4, curve 1). This is understandable since at an equilibrium concentration of e.g. 100 μmoles CMU per l($c/c_0$=0.08) only 0.4 μmole per g illite is adsorbed. This amounts to about 1 molecule per $10^5$ Å$^2$; interaction between adsorbed molecules is, therefore, improbable.

Although possibly of little significance, it may be attempted to estimate the adsorption energy from the calculated surface concentration, assuming a given thickness of the adsorbed layer. Thus accepting the thickness of the CMU molecule as the thickness of the adsorbed layer, one finds for the adsorption energy of CMU about 2 kcal per mole, whereas for similar assumptions the adsorption energy of chlorazine equals about twice this amount.

In acid environment the expected adsorption of the cations formed through proton association is indeed taking place.

Nevertheless it is hard to conceive at first sight that the observed increase in adsorption at pH values situated about 5 to 6 units above the pK value may be attributed entirely to the formation of cations. Possible deviations from theoretical expectations should then be explained by adsorption via SiOH-groups as was described by ILER (32). In order to estimate the energy that would have to be attributed to ILER's form of adsorption a trial calculation was set up for the adsorption of trietazine on Na-montmorillonite (cf. fig. I-5, curves 5 and 5'). If it is assumed that the ratio of Na- and H-ions in the double layer equals that in solution, the difference in pH between the solution in the neighborhood of the adsorbing surface and the equilibrium solution may be calculated. Next the concentrations of the monovalent and divalent cations are calculated in the neighborhood of the surface, making use of $pK_1 = 1.88$ and $pK_2 = 0$. These concentrations are then used in the calculation as a pseudo equilibrium concentration of the cations. Since these concentrations are very low in comparison to the Na-ion concentration, the amount of trietazine ions adsorbed in the double layer may be calculated with equations similar to equation [11]. If it is now assumed that at a pH of 10 both Coulomb adsorption and adsorption according to ILER are absent, the relation, f(g), between the concentration in equilibrium solution and the amount of trietazine adsorbed, may be calculated. Assuming furthermore that the calculated factor f(g) is pH-independent, one may now calculate the amount of ions adsorbed due to Van Der Waals forces with help of the equations [16], [24] and [25]. At the same time one finds the amounts of undissociated molecules adsorbed at the different values of the pH. Obviously one has to employ the pH in the equilibrium solution in order to calculate the amount of trietazine present as uncharged molecules. The results of the calculations are given in table II-3; it follows from this table that the calculated adsorption in the pH range 9 to 5 is indeed smaller than the experimental values. In the pH range 4 to 2.9 the calculated adsorption is much too high. This seems understandable since the calculated surface concentration equals 35 μmoles per l at a pH of 6 whereas it is increased to 707 μmoles per l at a pH of 4. This last concentration is in excess of the solubility of the neutral molecules and accordingly the empirical factor f(g) may be invalid for this situation. The differences between calculated and experimentally determined adsorption in the pH range 9 to 5 may in principle be attributed to the adsorption according to Iler. From the ratio of the calculated and experimental value of the amount adsorbed, the Iler adsorption energy is then estimated. The results of this calculation are also given in table II-3. From this table it follows

Table II-3. The adsorption of trietazine on Na-montmorillonite, in 0.06 N NaCl, as a function of the pH. The adsorption values are given in μmoles per gram

| pH in equilibrium dialysate | Calculated adsorption | | | | | | Measured adsorption | Adsorption energy according to the mechanism as described by Iler cal/mole |
|---|---|---|---|---|---|---|---|---|
| | molecules according to Van Der Waals forces | monovalent ions | | divalent ions | | total adsorption according to Coulomb and Van Der Waals forces | | |
| | | according to Coulomb forces | according to Van Der Waals forces | according to Coulomb forces | according to Van Der Waals forces | | | |
| 10.0 | 1.00 | – | – | – | – | 1.00 | 1.00 | – |
| 9.0 | 1.00 | – | – | – | – | 1.00 | 1.07 | 40 |
| 8.0 | 1.00 | – | – | – | – | 1.00 | 1.40 | 190 |
| 7.0 | 1.00 | – | 0.02 | – | – | 1.02 | 2.05 | 370 |
| 6.0 | 1.00 | – | 0.16 | – | – | 1.16 | 2.98 | 550 |
| 5.0 | 1.00 | 0.01 | 1.62 | – | 0.07 | 2.70 | 5.05 | 360 |
| 4.0 | 0.99 | 0.14 | 15.9 | – | 6.69 | 23.4 | 19.0 | – |
| 3.0 | 0.93 | 1.34 | 153 | 0.23 | 639 | 795 | 66.0 | – |
| 2.9 | 0.91 | 1.61 | 185 | 0.37 | 989 | 1180 | 72.5 | – |

that this energy is fairly low in the pH range 9 to 5. Although the energy of adsorption according to this mechanism could very well increase in strongly acidic environment no quantitative information is available for this range.

In figure I-2, in which the salt content was chosen as a variable, it is observed that the adsorption in the range of 0.005 to 0.2 N $CaCl_2$ decreases somewhat in the direction of increasing salt concentration. This may be explained by the fact that the pH in the double layer at a salt concentration of 0.005 N is about 0.8 units lower than at a level of 0.2; this would favor adsorption of chlorazine at the low salt concentration. At salt concentrations in excess of 0.2 N $CaCl_2$ one finds an ever increasing adsorption; in this range obviously the salting-out effect becomes dominant.

## 3.3. THE ADSORPTION OF ORGANIC ACIDS AND ANIONS

The theoretical considerations suggest that DNC, DNBP, 2,4-D, 2,4,5-T, MCPA, picric acid and picrolonic acid will interact with clay minerals in several manners. Thus negative adsorption of anions on the negatively charged planar sides, positive adsorption of anions on the positively charged edges and also adsorption of undissociated molecules should be considered.

As is shown in figure I-11 through –15 negative adsorption is indeed found at high pH values. Especially for Na-montmorillonite and Na-illite the observed values (Na-montmorillonite 0.053 μmole per g at pH 8 in 0.06 N NaCl; Na-illite about 0.010 μmole per g in 0.06 N NaCl) agree quite well with the calculated values. Thus taking the specific surface area of montmorillonite at $8 \times 10^6$ cm$^2$ per g and that for illite at $2 \times 10^6$ cm$^2$ per g one finds from equation [14] the values 0.050 μmole per g for Na-montmorillonite and 0.013 μmole per g for Na-illite. In figure I-16 the calculated and experimental values for the negative adsorption on Na- and Ca-montmorillonite are plotted as a function of the salt content.

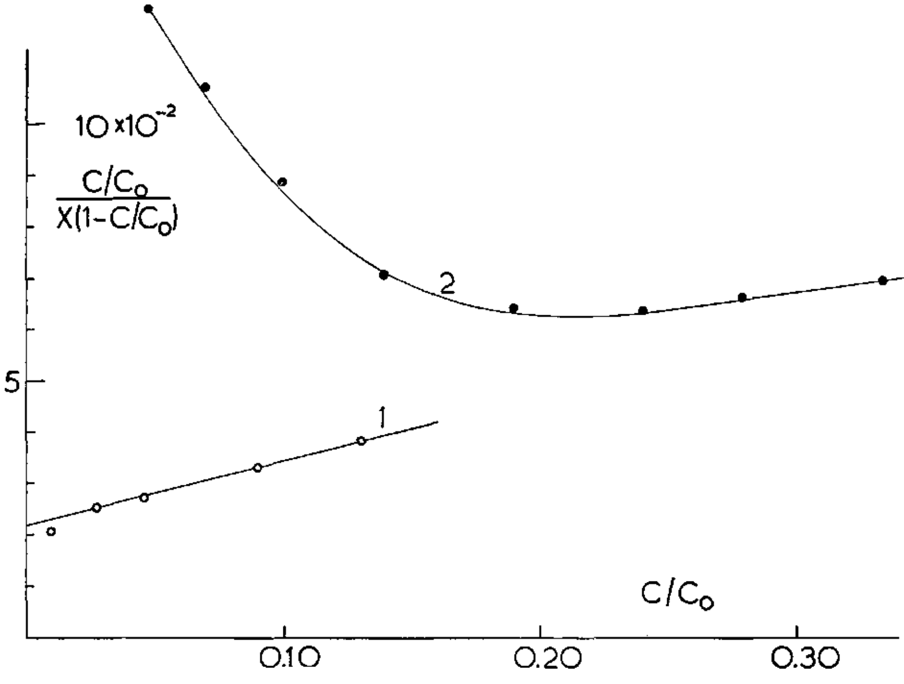
Is the agreement striking for Na-montmorillonite, for Ca-clay the observed negative adsorption is much smaller than the calculated value. This may be explained by the condensation of elementary clay platelets in larger units in the presence of Ca-ions as already mentioned in section 3.1. This condensation was suggested by van OLPHEN (45) on the basis of viscosity determinations in bentonite suspensions. Also BLACKMORE and MILLER (1) conclude from the measurements of the swelling pressure that the elementary clay platelets are combined into polyplates in Ca-montmorillonite. The number of plates per polyplate is estimated by these authors at 4 to 8. The measurements of negative adsorption discussed in Part I of this paper would suggest about 2 or 3 platelets per unit (experimental negative adsorption is about 40% of the theoretical value). The difference between the two methods may be explained by the consideration that the repeated compression occurring during the measurement of the swelling pressure increases the probability of association between the elementary platelets. It is interesting to note that a Na-montmorillonite, giving the correct value of the negative adsorption, after being exchanged into the Ca-form already shows a decreased negative adsorption of about 40%. This is so notwithstanding the fact that no compression, whatsoever, took place during this exchange. It could also be shown that the negative adsorption of the Ca-clay could not be influenced by subjecting the suspension to vibrational dispersion. This fact is confirmed by the observation that the increased Schlieren-effect of Ca-clay in comparison to Na-clay cannot be removed by this treatment.

For the kaolinite samples the accuracy of the observations was not sufficient to allow quantitative conclusions. The order of magnitude of the observed negative adsorption agrees with the calculated amount ($3 \times 10^{-3}$ μmole per g, cf. fig. I-15).

Positive adsorption of anions occurs at low pH values. From the appearance of the adsorption isotherms it is found that both the adsorbent-dependent and the adsorbate-dependent pH effects are present. Thus all isotherms on illite exhibit a change in character at a pH between 6 and 7 (cf. fig. I-12 through –14), whereas all isotherms of e.g. 2,4-D show a change of slope at a pH of about 4 (cf. fig. I-11, -12 and -14). As the pK value of 2,4-D is 2.80, this acid will be dissociated almost completely above pH 4. Accordingly it should be expected that the adsorption of this compound between pH 7 and 4 is caused by the adsorption of anions on positively charged edges. Below pH 4 an increasing portion of the 2,4-D will be present in the undissociated form; the adsorption in this range of pH may thus be attributed to the adsorption of uncharged molecules.

In figure II-2 the adsorption of undissociated DNC on illite (Winsum), at pH 3.4, in the presence of 0.06 N NaCl, is plotted according to the BET theory. The points in the range of $c/c_0$ between 0.03 and 0.13 lie on a straight line. The difference between heat of adsorption and heat of crystallization, $E_1$—$E_L$, calculated from this line amounts to 630 cal per mole. If it is assumed that the adsorbed molecules are spread over the entire surface area, the available area per molecule of DNC is 2000 Å$^2$. From structure models it can be estimated that the surface area of a DNC molecule is only about 55 Å$^2$. Accordingly the coverage of the clay surface by the DNC molecules in the first layer of adsorption is far from complete, unless it is assumed that the molecules are adsorbed on the much smaller edge surface. In view of the fact that the adsorption increases in the same direction as the total surface area, the latter assump-

FIG. II-2. The adsorption of DNC on different clay minerals, plotted according to the BET method



Curve 1: On illite (Winsum), 0.06 N NaCl, pH 3.4
Curve 2: On montmorillonite, 3.6 N NaCl, pH 7.0

tion seems untenable. Thus the adsorption of DNBP at pH 4, in 0.06 N NaCl and at an equilibrium concentration of 30 μmoles per l, on montmorillonite, illite (Grundite, L), illite (Winsum) and kaolinite (Drybranch) amounts to 1.80, 1.75, 0.42 and 0.011 μmoles per g, respectively; the corresponding surface areas are $9.0 \times 10^6$, $2.5 \times 10^6$, $4.0 \times 10^6$ and $0.5 \times 10^6$ cm² per g, respectively.

The adsorption of organic anions on positively charged edges was found only in the case of illite. The overall behavior of the organic acids is about the same. From the differences in adsorption energy between the dissociated and undissociated compounds, calculated from the ratio of the adsorbed amounts of the dissociated and undissociated form, it appears, however, that there are also some differences (cf. table II-4). This calculation, executed at one pH unit above the pK, is complicated by the fact that the adsorbing surface area is different for both forms of the acid, the molecules being adsorbed on the planar surface and the ions on the edge surface. In table II-4 the edge surface is approximated as 20% of the total surface area. It follows from the table that the difference in adsorption energy for DNBP is roughly independent on the type of illite. For the various acids the values thus calculated are different.

TABLE II-4. The difference between the adsorption energy of organic acids in ionic and molecular form

| Type of illite | Type of salt (0.06 N) | Organic acid | Adsorption energy of molecular form minus adsorption energy of ionic form. cal/mole |
|---|---|---|---|
| Grundite, M | NaCl | 2,4–D | 400 |
| Grundite, M | $CaCl_2$ | DNBP | 1320 |
| Grundite, L | NaCl | picric acid | —740 |
| Grundite, L | NaCl | DNBP | 1250 |
| Grundite, L | $CaCl_2$ | DNBP | 1060 |
| Winsum | $CaCl_2$ | 2,4,5–T | 1070 |

The observations of FRIPIAT (21) and CASHEN (12) indicated that one should also expect positive adsorption of organic anions on kaolinite; this was not borne out by the experiments. To elucidate this matter it was attempted to adsorb Cl- and $I^{131}$-ions on some clay minerals in order to establish the amount of positive charge present. With these experiments, in contrast to the experiments with the organic anions, no other anions were present. The adsorbed amount should then equal the amount of positive charge, provided Coulomb forces are the main source of attraction for these ions. From table I-8 it appears, however, that the anion adsorption is strongly dependent upon both the concentration and pH and upon the type of anion. Thus the anion adsorption is subject to Coulombic as well as to non-Coulombic forces (cf. the anion adsorption on the mercury surface). The influence of concentration and pH indicates that the surface charge must be due to an association-dissociation reaction of protons. If it is finally taken into account that the entire OH-groups at the edges are also replacable by e.g. F-ions (WEISS et al. 59), it is obvious that for clay minerals the anion exchange capacity is not a material property, as is e.g. the cation exchange capacity. The specificity of anion adsorption is also demonstrated by the fact that the amount of DNBP adsorbed on illite is hardly influenced by a replacement of the Cl-ions in the systems by $PO_4$- or $SO_4$-ion (cf. table I-7); on the other hand the adsorbed amount of picrolonic acid is influenced strongly by the addition of the polyvalent anion HPAN (cf. fig. I-8, curves 5 and 6).

As was indicated in section 1.3. the activity corrections resulting from high salt contents should lead to an increased adsorption under those circumstances. These effects are demonstrated for DNC and DNBP in fig. I-11 and -16; apparently this effect is pH dependent, i.e. the closer the pH approaches the pK value, the higher is the adsorption. This would indicate that the adsorption at high salt content takes place in the form of undissociated molecules. If the adsorption of DNC on Na-montmorillonite, at a salt content of 3.6 N NaCl, is plotted according to the BET theory the resulting line is curved (cf. fig. II-2). Thus the adsorption energy is in this case a function of the amount already adsorbed. This could be due to differences in packing when comparing the high salt adsorption with low salt adsorption.

### 3.4. Some general considerations

As could have been expected the experimental observations indicate that although the adsorption of herbicides may be explained in a qualitative manner, the quantities adsorbed are mainly determined by specific interaction forces of, a priori, unknown magnitude. This specificity makes it virtually impossible to extrapolate to general predictions in a quantitative sense. Thus the present study should perhaps be considered as an outline of experimental procedures that may be used to study particular cases. At the same time it may serve as a preview of the phenomena to be expected both with regard to kind and order of magnitude.

# 4. PRACTICAL IMPLICATIONS

The yield of crops may be depressed severely by weeds. Before the second world war this decrease in yield was estimated for the U.S.A. at 25% (48); at present the estimate for the Netherlands runs between 5 and 10% (47). Accordingly weed-control is considered to be of prime importance in agriculture. After the discovery of more or less selective herbicides the use of chemicals in weed-control has increased considerably.

Herbicides may be divided into two groups: viz., contact herbicides and systemic herbicides. Contact herbicides are sprayed on leaves and stems, causing the death of these parts of the plants. Penetration of the contact herbicides into the soil has no direct influence on the underground parts of the plant; the roots remain intact. The action of systemic herbicides, on the other hand, results from uptake by the roots and/or through the leaves and subsequent transport to other parts of the plant. Without causing a straight kill of plant cells these chemicals disturb the metabolism of the plant, resulting in abnormal growth processes and eventually in death of the plant. In case the herbicides are taken up through the root system it will be necessary to bring the concentration of the herbicides in the soil solution at a level sufficiently high to allow the uptake of the amount of herbicide causing death of the plants.

Due to increased cost of labor it should be expected that the application of herbicides will increase continuously. The increasing use of herbicides and other pesticides brings up the question whether accumulation of these compounds in soil could occur, eventually leading to a level causing yield depression of crops. Obviously the data given in this publication do not suffice to give an answer to this question. Adsorption on clays is certainly not the only type of accumulation occurring in soils. Also the organic matter fraction of the soil will adsorb these chemicals; furthermore leaching and biological and chemical breakdown must be considered.

In table II-5 an example is given of the amounts of herbicide that, in a given case, will be adsorbed by the clay minerals in the soil. Although not entirely satisfactory, for this calculation it was assumed that the herbicides are distributed homogeneously over the furrow slice and that no adsorption on other compounds were to take place. In the example discussed the depth of the furrow slice was taken as 20 cm, the bulk density was chosen at 1.5 and the moisture content at 20%. Under these circumstances the concentration of the herbicides added would vary between 8 and 30 μmoles per l. Accordingly the adsorption curves, as given in Part I, give a fair impression of the situation occurring. The pH given refers to the soil solution. Usually this pH value is not known and instead the pH of a soil suspension in water, in 0.1 N KCl or 0.01 N $CaCl_2$ is given. The electrolyte concentration in the soil solution is about 0.02 N and accordingly the pH measurements executed in presence of 0.01 N $CaCl_2$ should give the best correlation with the values given in table II-5. In addition values are given of the concentrations of these herbicides which would occur in the soil solution. Although the adsorption on materials other than clay (i.e. organic matter fraction) may be considerable in certain cases, the tabulated values should at least

TABLE II-5. Predicted values of the adsorption of herbicides on clay minerals present in the soil

| Herbicides | Dose kg/ha | Clay mineral present in the soil | Concentration in the soil solution in mg/l pH | | | | Amount adsorbed in percent pH | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 4.6 | 5.5 | 6.4 | 7.3 | 4.6 | 5.5 | 6.4 | 7.3 |
| DNC | 4 | illite | 0.027 | 0.065 | 0.19 | 6.7 | 99.6 | 99.0 | 97 | 0 |
| | | kaolinite | 1.5 | 2.5 | 6.7 | 6.7 | 77 | 63 | 0 | 0 |
| | | montm. | 0.031 | 0.059 | 0.18 | 6.7 | 99.5 | 99.1 | 97 | 0 |
| DNBP | 1 | illite | 0.007 | 0.016 | 0.048 | 1.7 | 99.6 | 99.0 | 97 | 0 |
| | | kaolinite | 0.39 | 0.63 | 1.7 | 1.7 | 77 | 63 | 0 | 0 |
| | | montm. | 0.008 | 0.015 | 0.044 | 1.7 | 99.5 | 99.1 | 97 | 0 |
| 2,4-D<br>2,4,5-T<br>MCPA | 1 | illite | 0.048 | 0.048 | 0.094 | 1.7 | 97 | 97 | 95 | 0 |
| | | montm. | 1.7 | 1.7 | 1.7 | 1.7 | 0 | 0 | 0 | 0 |
| CMU<br>DCMU | 1 | illite | 0.054 | 0.068 | 0.073 | 0.079 | 96 | 96 | 96 | 95 |
| | | montm. | 0.024 | 0.028 | 0.030 | 0.032 | 98.6 | 98 | 98 | 98 |
| Trietazine<br>Simazine<br>Chlorazine | 1.5 | illite | 0.007 | 0.014 | 0.024 | 0.037 | 99.7 | 99.4 | 99.0 | 98.6 |
| | | kaolinite | 0.037 | 0.072 | 0.14 | 0.14 | 98.6 | 97 | 95 | 95 |
| | | montm. | 0.001 | 0.004 | 0.007 | 0.010 | 100.0 | 99.8 | 99.7 | 99.6 |

indicate the minimum amount of adsorption and the maximum concentration in the soil solution.

It follows from table II-5 that the adsorption on the clay minerals may vary between 0 and 100%. Accordingly, not considering chemical and biological breakdown, the possibility of accumulation should be considered. This will be especially the case with the systemic herbicides: simazine, chlorazine, trietazine, CMU (monuron) and DCMU (diuron). This accumulation deserves attention, especially because it is known that these compounds will also be adsorbed on the organic matter fraction in the soil. Furthermore the differences in adsorption, at varying pH values, are noteworthy. It should be kept in mind, however, that during the growing season variations in pH are mainly limited to those occurring as a result of the fluctuations in salt concentration following changes in moisture content. The application of lime will usually be limited to periods outside the growing season. The influence of the type of clay mineral present is considerable. Generally the adsorption on montmorillonite exceeds that on illite, whereas the least adsorption takes place on kaolinite.

Considering the data published one should expect a loss in biological activity of application of herbicides on soils rich in the investigated clay mineral. This is in agreement with practical experiences. Soils high in adsorptive capacity require higher dosage of most soil-active herbicides than lighter soils. Naturally the organic matter content of the soil should also be considered in estimating the relative loss in activity of herbicides applied.

# SAMENVATTING

In dit proefschrift zijn de resultaten beschreven van een onderzoek over de adsorptie van verschillende organische verbindingen, meest herbiciden, aan kleimineralen.

In deel I wordt een overzicht gegeven van de structuur der kleimineralen montmorilloniet, illiet en kaoliniet. Deze mineralen bestaan uit negatief geladen plaatvormige deeltjes van colloïdale dimensies; de randen kunnen onder bepaalde omstandigheden positief geladen zijn.

Uit het literatuuroverzicht blijkt dat de daar beschreven adsorptiemetingen vrijwel geen conclusies omtrent de adsorptie van herbiciden aan kleimineralen mogelijk maken. De metingen werden uitgevoerd met de sterke base methyleenblauw, met de zwakke basen CMU, DCMU, simazin, chlorazin en trietazin en met de zuren 2,4-D, 2,4,5-T, MCPA, DNC, DNBP, pikrinezuur en pikrolonzuur (zie voor de volledige naam der herbiciden tabel I-3). De resultaten van deze metingen zijn voor het grootste deel grafisch weergegeven.

In deel II wordt een theoretische verklaring van de verschillende adsorptietypen gegeven. De adsorptie van herbiciden aan kleimineralen kan opgevat worden als een combinatie van adsorptie van ionen in electrische dubbellagen en de adsorptie van ionen en moleculen door specifieke krachten. De sterke base methyleenblauw werd steeds sterk geadsorbeerd; in verschillende gevallen trad omlading op. Dit wijst erop dat ook andere dan Coulomb krachten een belangrijke rol spelen. De adsorptie van methyleenblauw kan zelfs met de theorie van BRUNAUER, EMMET en TELLER beschreven worden, dit duidt erop dat de adsorptieenergie constant is en dus groot is ten opzichte van de Coulomb energie.

De adsorptie van de zeer zwakke basen vindt in zuur milieu plaats in de vorm van positieve ionen. Uit een berekening blijkt echter dat ook hier andere dan Coulomb krachten aanzienlijk zijn.

De met behulp van dubbellaag theorieën berekende negatieve adsorptie van organische anionen aan het negatief geladen kleioppervlak is in overeenstemming met de experimenteel gevonden waarden. Positieve adsorptie van anionen werd geconstateerd aan illiet in zuur milieu; deze adsorptie werd toegeschreven aan de aanwezigheid van positieve randladingen. Ook in ongedissocieerde toestand werden de genoemde zuren geadsorbeerd, nu echter onder invloed van van der Waals krachten. Zowel de aanwezigheid van positieve randladingen, als de mate van dissociatie der zuren is afhankelijk van de pH. Door de geadsorbeerde hoeveelheid, bij een constante evenwichtsconcentratie, uit te zetten als functie van de pH werd dan ook zowel een adsorbens-afhankelijk als een adsorbaat-afhankelijk pH effect gevonden.

Uit de experimentele gegevens kan afgeleid worden dat in de bodem accumulatie van verschillende herbiciden mogelijk is.

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