ABSTRACT

Ph.D SINNATHAMBY KADIRGAMATHAIYAH Soil Science

ROLE OF ALUMINUM AND IRON HYDROXY COMPOUNDS IN THE ADSORPTION OF ORGANIC MATTER BY MONTMORILLONITE CLAY

Adsorption and desorption of two soil organic matter preparations on bentonite clay artificially coated with Al or Fe hydroxy compounds were studied. Reactions of organic matter with polynuclear or polymeric hydroxy Al, Fe compounds in aqueous solutions and on clay surfaces were also investigated using infra-red absorption spectroscopy, X-ray diffraction and electron microscopy.

Organic matter was adsorbed on both the external planar and edge surfaces but not in the interlamellar spaces of the Al, Fe hydroxy-clays. Adsorption of organic matter conformed approximately to the Langmuir isotherm. Approximately one-fifth to one-quarter of the adsorbed organic matter was not desorbed by Na_2CO_3 but was completely desorbed by NaOH. Organic matter was found to have an inhibitory or retarding effect on the formation of gibbsite. A coordination mechanism (anion penetration) was suggested in addition to electrostatic interaction, hydrogen bonding and Van der Waals forces, to account for the high adsorption of organic matter by hydroxy Al or hydroxy Fe-bentonite.

Short Title

ORGANIC MATTER - CLAY INTERACTIONS

S.Kadirgamathaiyah

ROLE OF ALUMINUM AND IRON HYDROXY COMPOUNDS IN THE ADSORPTION OF ORGANIC MATTER BY MONTMORILLONITE CLAY

by

Sinnathamby Kadirgamathaiyah

A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Department of Soil Science
McGill University
Montreal

July 1969

Suggested short title

ORGANIC MATTER-CLAY INTERACTIONS

Kadirgamathaiyah

ABSTRACT

Ph.D. SINNATHAMBY KADIRGAMATHAIYAH Soil Science

ROLE OF ALUMINUM AND IRON HYDROXY COMPOUNDS IN THE ADSORPTION OF ORGANIC MATTER BY MONTMORILLONITE CLAY

Adsorption and desorption of two soil organic matter preparations on bentonite clay artificially coated with Al or Fe hydroxy compounds were studied. Reactions of organic matter with polynuclear or polymeric hydroxy Al, Fe compounds in aqueous solutions and on clay surfaces were also investigated using infra-red absorption spectroscopy, X-ray diffraction and electron microscopy.

Organic matter was adsorbed on both the external planar and edge surfaces but not in the interlamellar spaces of the Al, Fe hydroxy-clays. Adsorption of organic matter conformed approximately to the Langmuir isotherm. Approximately one-fifth to one-quarter of the adsorbed organic matter was not desorbed by Na_2CO_3 but was completely desorbed by NaOH. Organic matter was found to have an inhibitory or retarding effect on the formation of gibbsite. A coordination mechanism (anion penetration) was suggested in addition to electrostatic interaction, hydrogen bonding and Van der Waals forces, to account for the high adsorption of organic matter by hydroxy Al or hydroxy Fe-bentonite.

ACKNOWLEDGEMENTS

The author expresses his sincere thanks and appreciation to Professor A. F. Mackenzie, Chairman, Department of Soil Science, Macdonald College of McGill University, for the encouragement and advice given to him during the study, and valuable suggestions in the preparation of the thesis.

The author is deeply indebted to Professor B. P. Warkentin, Department of Soil Science, for the very helpful discussions in general and advice on X-ray diffraction; Professor J. F. G. Millette, Department of Soil Science for helpful suggestions; Professor J. W. F. Costerton and Mrs. J. M. Weilandt, Department of Microbiology, Macdonald College, for the excellent electron micrographs.

Thanks are also due to Dr. C. R. Frink, Connecticut Agricultural Experiment Station, New Haven, U.S.A., for a discussion on aluminum interlayering of clays and to Mrs. May Couture for typing this thesis.

The author gratefully acknowledges the scholarship from the Canadian Commonwealth Scholarship and Fellowship Committee, which made this work possible.

CONTRIBUTIONS TO KNOWLEDGE

1. Organic matter was adsorbed on both the planar and edge faces of hydroxy Al, Fe-bentonites but not in the interlayer space.

2. Adsorption of organic matter on hydroxy Al, Fe-bentonites conformed approximately to the Langmuir adsorption isotherm. However, deviations were also observed at both low and high concentrations of organic matter.

3. Eighteen to thirty per cent of organic matter adsorbed by hydroxy Al, Fe-bentonites was not desorbed by 0.5N Na_2CO_3 but was desorbed by 0.5N NaOH.

4. Organic matter had an inhibitory or retarding effect on the formation of X-ray crystalline $Al(OH)_3$. Presence of organic matter on the external surfaces of hydroxy Al-bentonite did not affect the formation of gibbsite from interlayer Al-hydrous oxide.

5. A coordination mechanism (anion penetration) has been proposed to account for part of the organic matter adsorbed by hydroxy Al, Fe-bentonites.

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

Figure Page

I. INTRODUCTION

Organic matter, a vital component of soils, is present variously linked to the mineral constituents. The linkage ranges from simple physical entrapment to multiple chemical bonding. The complexity and importance of the organo-mineral complex was well described by Jacks (1963) in the following words, ". . . the union of mineral and organic matter to form the organo-mineral complex (is) a synthesis as vital to the continuance of life as, and less understood than photosynthesis."

A large part of the organic matter occurs tightly bound to the inorganic soil surfaces or co-precipitated with the oxides and hydroxides of Al, Fe, Si and Mn. Bonding could occur at clay surfaces and at the surface of oxides and hydroxides, present as a separate phase or as coatings on clay surfaces. In natural soils, the surface of the clay minerals may not generally be "clean." Clay-organic matter complexes account for 52-98 per cent of the total carbon in different soils (Greenland 1965a), the highest value being for lateritic red earth, where large amounts of Al, Fe hydroxy compounds and oxides are present.

At least a part of the humic substances not extractable with alkalis (humin) is considered to exist in firm association with clays and sesquioxides (Dubach and Mehta 1963). It is becoming increasingly evident that the coatings of Al and Fe hydroxy compounds on clay surfaces largely influence their physico-chemical properties (Coleman and Thomas 1967; Davey and Low 1968). Van der Waals-London forces, coulombic attraction, coordination and chelation have been suggested to explain clay-organic matter bonds. The exact manner in which the organic matter is bonded to hydroxy Al and Fe compounds present as coatings on clay surfaces is not well established.

This study was undertaken to investigate the influence of hydroxy Al and Fe polymeric or polynuclear compounds deposited under laboratory conditions on montmorillonite clay surfaces on the adsorption of soil organic matter by montmorillonite. Adsorption and retention characteristics, sites of adsorption, reactions with hydroxy Al and Fe compounds in solution and on clay surface were studied and possible mechanisms of adsorption were examined in the light of the results obtained.

II. REVIEW OF LITERATURE

II.1. General characteristics of organic matter

Soil organic matter has been broadly divided into non-humic and humic substances. The non-humic group consists of compounds of definite chemical characteristics such as amino acids, proteins, carbohydrates, fats, waxes, low molecular weight acids, etc. Humic substances are a series of brown to black high molecular weight polymers generally with an aromatic nucleus and possibly with aliphatic side chains and formed either by secondary synthesis of decomposed products or degradation and alteration of the original residues or a combination of both processes. Being more susceptible to microbial attack, non-humic substances have a comparatively shorter life span in soils than the more stable humic substances (Kononova 1966; Dubach and Mehta 1963).

Humic compounds have been further subdivided on solubility characteristics into humic acid, fulvic acid and humin. Humic acid, the high molecular weight fraction, is insoluble in acids and soluble in alkalis. Fulvic acid is of low molecular weight and soluble in both acids and alkalis. Humin fraction is insoluble in acids and alkalis, and Kononova (1966), while considering this fraction to be closely related to humic acids, attributed the loss of solubility not to the alteration in the nature of the humic acid but to the firmness of the linkage to the mineral part in soils. Using fractional precipitation, electrophoresis and chromatography, it has been demonstrated that the humic substances are heterogeneous in nature and could be separated into a number of fractions. The humic and fulvic acids are very much related and are members of a system of polymers. Reviewing the current literature on this particular aspect, Kononova (1966) concluded that the process of acidification of alkaline extracts is not a means of separating fundamentally different groups - fulvic and humic acids - but a way of fractionating humic acids into different molecular weight fractions. She further concluded that "the division of humus substances into humic and fulvic acids as individual groups has lost its importance." However, it should be pointed out that apart from molecular weight difference, there exist differences in the number and ratio of functional groups between humic and fulvic acids (Schnitzer 1965).

While Greenland (1965b) cited evidence to show that humic acids do not behave like typical polyelectrolytes, Mukherjee and Lahiri (1956), Piret et al. (1960), Ling Ong and Bisque (1968) obtained evidence to show that humic acids behave like polyelectrolytes in aqueous solutions. The latter authors explained the behaviour of peat humic acids towards salt solutions assuming coiling and uncoiling as in the case of polyelectrolytes (Fuoss and Strauss 1948; Fuoss and Cathers 1949).

II.1.1. Functional groups and their arrangement

The presence of carboxyls, phenolic and alcoholic hydroxyls, ketonic carbonyl groups, methoxyls ester groups, amino groups, has been well established by titrimetric, methylation, acetylation, esterification, saponification and I.R. absorption procedures (Gillam 1940; Wright and Schnitzer 1959; Broadbent and Bradford 1952; Dubach and Mehta 1963; Schnitzer and Gupta 1964; Schnitzer 1965; Felbeck, Jr. 1965; Kononova 1966; Theng _et_ _al_. 1966; Theng and Posner 1967). The presence of quinone groups is rather controversial. Knowledge on the structural arrangement of these groups is very limited.

All the acidic groups are not of the same strength.

Variation in the pk values both between and within molecules has been reported (Dubach and Mehta 1963; Posner 1966). Some tentative structures have been proposed for humic acid but have not been proven beyond doubt (Kononova 1966).

Wood et al (1961) obtained I.R. spectroscopic evidence for the formation of mixed anhydrides and cyclic anhydrides by heating humic acid from lignite with acetic anhydride. The nature of the anhydride formed was not known but the authors considered the possibility of 5, 6 and 7 membered ring anhydrides. Falk and Smith (1963) also reported cyclic anhydride formation from lignite humic acid. Wright and Schnitzer (1961) obtained I.R. absorption bands characteristic of anhydrides for the product obtained by heating an organic matter preparation for 50 hours at 170°C. They found that not more than one-tenth of the carboxyl groups in the organic matter preparation was recovered in the anhydrides. Wagner and Stevenson (1965) reported that one-third of the carboxyl groups in a soil humic acid occurred in positions close enough to form cyclic anhydrides. The anhydrides formed were rather unstable under normal humidity conditions compared with stable phthalic anhydride. The latter authors also observed that some groups that could be hydrolysed with 6 N HCl at 105°C blocked the formation of anhydride. Cifrulak (1967) obtained I.R. spectorscopic evidence for the presence of a phthalic diester with a long side chain in a benzene-methanol-acetone extract of soil organic matter.

Complexing and chelating ability of humic substances was considered to be largely determined by the presence of hydrophilic groups in the side chain (Kawaguchi and Kyuma 1959; Kononova 1966). Studies on reactions of metal ions with organic matter have shown the presence of chelating or complexing groups. Chelating groups may be carboxyl, hydroxyl, keto, amino, imino, thioether, etc. An extensive review of this aspect was given by Mortensen (1963). Thus despite the fact that the exact structural arrangement of the functional groups is not known, there exist some functional groups which are so placed that formation of coordination complexes and chelates with metal ions is possible. Tartaric acid and pyrocatechol were considered to be ordinary decomposition products of organic material (Kononova _et_ _al_. 1964). Whether the same kind of functional groups arrangement exists in humic substances is not known.

II.1.2. Organic matter-clay interactions

While it is known that in addition to the clay-humus complex, humic material in soils could occur as humates, organo-metal complexes and gels mixed or co-precipitated with Al, Fe hydroxy compounds, literature relevant only to clay-organic matter interactions is reviewed here.

II.1.2.1. Adsorption characteristics

(a) Components of adsorbate

Soil organic matter is a heterogeneous system and it is therefore natural to expect the different components to be adsorbed in varying amounts and degree. Evans and Russell (1959) observed that only a small percentage of the added organic carbon of both humic and fulvic acids was adsorbed by bentonite clay and the re-extracted adsorbed portion remained highly adsorbable. Greenland (1956) showed that in contrast to humic acids, soil polysaccharides were adsorbed in larger amounts by montmorillonite.

(b) Adsorption isotherms

Jung's (1943) adsorption studies showed that all the organic carbon present in solution was adsorbed up to the level of adsorption saturation. He felt that the adsorption of humus materials by clays could be expressed better by a hyperbolic function than by an adsorption isotherm. Evans and Russell's (1959) calculation of Myers' (1937) data showed that 90 per cent of the added composted lucerne carbon was adsorbed in the acid systems and 70 per cent in the Ca-systems. A value of 20 per cent adsorption for humic acid and 23-14 per cent for fulvic acid on bentonite was obtained by Evans and Russell (1959) in their studies. Demolon and Barbier (1929) obtained an asymptotic curve for the adsorption of NH_4-humate on Ca-brick earth. A similar result was obtained by Evans and Russell (1959) for humic and fulvic acids on K-saturated montmorillonite. In contrast to other reports quoted above, the latter authors obtained fairly linear isotherms over the concentration range they used for Ca and H bentonites for both humic and fulvic acids. Saini and MacLean (1966) found that adsorption of soil polysaccharides on kaolinite conformed to the Langmuir adsorption isotherm. Conformity of adsorption to Langmuir isotherm was earlier observed by Mortensen (1957, 1962) for polyelectrolytes, who interpreted it as an indication of monolayer adsorption. However, Saini and MacLean (1966) pointed out that approximate conformity to Langmuir isotherm need not necessarily mean monolayer adsorption.

(c) pH and adsorption

Adsorption of humic and fulvic acids on bentonite was found to behave the same way with change in pH (Evans and Russell 1959). A sharp fall in adsorption was observed as the pH increased from 3 to 6. Adsorption slightly increased when the pH was higher than 7. The authors explained increased adsorption below pH 4 as due to flocculation by aluminum ions. They had to face an apparent inconsistency in that humic acid which is more susceptible than fulvic acid to flocculation by aluminum ions was adsorbed less in acid systems. Martin and Reeve (1960) compared adsorptions on Na-H bentonite and Al-bentonite. While the adsorption of humus material on Na-H bentonite was appreciable only at pH 2, above which there was slight or negligible adsorption, the Al-bentonite continued adsorbing appreciable amounts (though decreasing) up to pH 6, giving slightly less than 50 per cent adsorption of added carbon at pH 6. Greenlands' (1956) study on adsorption of polysaccharides on H-Ca montmorillonite indicated an interesting variation with pH. A maximum in adsorption was observed between pH 4 and 5. The adsorption then decreased as the pH was increased to 6 and again increased when the pH was greater than 6. He attempted to explain these observations by postulating different mechanisms. Maximum between pH 4 and 5 was considered due to complex formation with aluminum and the increase above pH 6 due to precipitation of the polysaccharides as insoluble Ca-salts.

(d) Nature of cations

Polyvalent cations (e.g., Al, Fe, Ca) on exchange sites were observed to promote adsorption of organic matter and polyelectrolytes by clays (Khan 1950; Sen 1960; Evans and Russell 1959; Martin and Reeve 1960; Kobo and Fujisawa 1964; Mortensen 1957, 1962; Saini and MacLean 1966). Adsorption of polysaccharides was higher with Fe than with Al saturated kaolinite (Saini and MacLean 1966). While Khan (1950) observed no difference between H and Ca clays, Evans and Russell (1959) reported that Ca bentonite adsorbed more humic acid than H-bentonite and H-bentonite adsorbed more fulvic acid than Ca-bentonite. In addition to the possibility of bridge linkages and complex formation, Mortensen (1959) and Ahlrichs (1962) suggested that the polyvalent cations were effective in reducing the zeta potential of the polymer and clay so that a closer approach was possible.

(e) Al, Fe hydrous oxides

The presence of Al^{3+} ions on H-resin treated clays is well established (Aldrich and Buchanan 1958). It is inevitable that Al-hydroxy compounds are formed when such clays are neutralised (wholly or partially) with alkalis (Davey and Low 1968). Evans and Russell (1959) recognised this aspect of Al release and hydrolysis and suggested that not only ionic Al and Fe but also their hydroxylated species could play an important role in the adsorption of organic matter by clays. These workers also observed that bentonite brought to pH 9.0 from the acid condition (i.e., after resin treatment) adsorbed more than the native bentonite at the same pH.

Kobo and Fujisawa (1964) reported that the presence of "active" sesquioxides enhanced adsorption of humic acids by clays. The term "active" sesquioxides used in Japanese literature was considered to be synonymous with amorphous sesquioxides (Mitchell et al 1964). Aleksandrova and Nad (1958) observed that freshly prepared amorphous Al or Fe hydroxides were more efficient in adsorbing humic substances than old crystalline forms. Levashkevich's (1966) experiments showed that Al-hydroxide gel adsorbed more humic acid than its own weight expressed as Al_2O_3. He also observed that iron hydroxide adsorbed 64-84 mg humic acid per 100 mg Fe_2O_3. Adsorption studies with humic and fulvic acids showed that gibbsite adsorbed maximum amount around pH 5 and adsorption decreased with increasing pH. Lepidocrocite exhibited a maximum around pH 3 and here, too, the adsorption decreased with increasing pH. However, significant amounts were adsorbed by these two crystalline hydroxides even at pH 7 (Evans and Russell 1959).

II.1.2.2. Sites of adsorption

Knowledge of the sites of adsorption has been gathered largely from quantitative adsorption studies, X-ray diffraction data and electron micrographs. Considerable information on this aspect has also been obtained from the study of anionic polyelectrolyte-clay systems. Data obtained with organic cations may not be very relevant to organic matter as the positive charges, if any, present on free amino groups in organic matter are negligibly small (Russell 1961). Evans and Russell (1959) observed no marked inflection points corresponding to amino groups in the potentiometric titration and spectrograph-adsorption curves of humic and fulvic acids they used.

In most of the adsorption studies, suggestion has been made that the adsorption takes place at the edge face of the clay crystal. Such an idea is based on the fact that edge positive charges on clays are responsible for holding the negatively charged organic matter or polyelectrolyte (Ruehrwein and Ward 1952; Warkentin 1956; Emerson 1956a,b; Mortensen 1962; Ahlrichs 1962). Ahlrichs (1962) observed that expanded forms of montmorillonite adsorbed more than the non-expanded form. He inferred from this that the space around the edges may be limiting the adsorption of large polymers.

Evidence for the adsorption of humic substances in the interlamellar spaces of montmorillonite is very controversial. A number of X-ray studies on humic matter - montmorillonite complexes showed no evidence of penetration (Sedletsky and Tatarinova 1941; Jung 1943; Aleksandrova and Nad 1958; Evans and Russell 1959). Khan (1946, 1950) observed penetration of humic substances into interlamellar space. Schnitzer and Kodama (1967) found that fulvic acid entered the interlamellar space at low pH values and sorption decreased with increasing pH. Ahlrichs (1962) obtained no evidence of interlayer adsorption of anionic polyelectrolytes on montmorillonite. In contrast to the humic substances, soil polysaccharides were found to be adsorbed in large amounts in the interlamellar spaces of montmorillonite (Dubach _et al_ 1955; Greenland 1965b).

The newly developing technique of electron microscopy has been used by a few workers to study the sites of adsorption. Kroth and Page (1946) inferred from their electron micrographs that organic matter was homogeneously adsorbed on all surfaces of bentonite particles. Their photographs are rather difficult to interpret since no mention was made of the removal of unreacted free organic matter. Electron micrographs of Beutelspacher (1955) indicated that humic acid was attached only to the edges of kaolinite. Edge-face linkage to polyelectrolytes has been observed also in the case of kaolinite (Kittrick 1965). Greenland (1965b) mentioned that the electron micrographs of Flaig and Beutelspacher (1951) have been interpreted to mean that the association between montmorillonite and humic acids is through the intermediary of Al or Fe oxides, Whether this occurs on the edge face or planar surface is not clear.

II.1.2.3. Clay-organic matter linkage

Humic compounds are negatively charged and it is highly improbable that they are held to the clay surface by physical adsorption forces alone. Greenland and Ford (1964) observed that ultrasonic dispersion of soil in heavy liquids separated only a small portion of the humic material from the mineral part, indicating the existence of chemical bonds. Physical adsorption, hydrogen bonding, coulombic interaction (including cation bridging) coordination and complex formation with exchangeable cations and hydrous oxides have been suggested as possible mechanisms of organic matter - clay interaction.

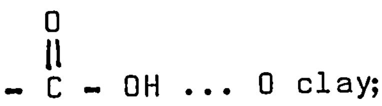
II.1.2.3.1. Physical adsorption

Physical adsorption is due to Van der Waals-London forces (the summation of charge-dipole, dipole-dipole, dipole-induced dipole, induced dipole-induced dipole interactions). These forces, though weak by themselves, could considerably augment other forces of bonding. Strength of bonding by Van der Waals forces largely depends on the size and shape of the adsorbed molecule, which in turn determines the number of contacts (Greenland 1965a). This view is supported by the fact that uncharged polymers once adsorbed are extremely difficult to desorb (Emerson 1963; Greenland 1963; Greenland 1965a). Studies with amino compounds with different number of carbon atoms showed that bond strength was greater with larger cations (Greenland 1965a). Large cations are more strongly adsorbed and difficult or impossible to replace with smaller cations due to Van der Waals forces (Grim 1953).

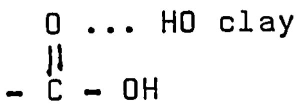
II.1.2.3.2. Hydrogen bonding

The hydrogen bond, a universal one present in all biological systems, is a weak bond which can be both formed and broken easily (Pauling 1960). There exists an unanswered question as to whether adsorption due to H-bonding is physical or chemical adsorption (Bailey et al 1968). Edsall and Wymann (1958) considered that hydrogen bonds under suitable conditions could be quite strong and could remain unbroken over a wide range of pH values.

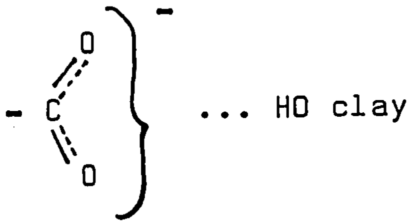
Three types of H-bonding of carboxyl group (COOH and COO^-) to clay surface are possible.



$$-\overset{O}{\overset{\|}{C}}-OH \ldots O\ \text{clay};$$



$$-\overset{O\ \ldots\ HO\ \text{clay}}{\overset{\|}{C}}-OH \quad ;$$



I

II

III

Sheraga (1961) considered the existence of the above types of hydrogen bonds in proteins (i.e., between COOH, COO^- and phenolic OH groups). In the second and third type the OH of the clay (pure) surface could be the OH attached to an edge Al or one of the few surface OH that may be found on the planar surface of montmorillonite (Van Olphen 1963).

The first type is easily broken at higher pH values as the carboxyl group ionises. Second and third types can be quite stable even at higher pH values. Emerson (1956a) considered that the H-bonds between clay and polyelectrolytes could be broken with strong alkalis.

Hydrogen bonding of polymer carboxyl to clay edge hydroxyls has been proposed by several workers (French et al 1954; Emerson 1955, 1956a, 1956b; Holmes and Toth 1957; Kohl and Taylor 1961; Ahlrichs 1962). Kohl and Taylor (1961) and Ahlrich (1962) observed a shift in the C = O stretching frequency by 0.05 µ or more towards longer wave length, when organic acids, ketones and polyelectrolytes were adsorbed on H or Ca-bentonite. These authors interpreted this shift as evidence of H-bonding between the carboxyl group and clay edge hydroxyls. However, they did not observe any shift in the OH stretching frequency to lower values nor the OH deformation frequency to higher values. These shifts are characteristic when a hydroxyl group is involved in H-bonding (Bellamy 1958). Kohl and Taylor (1961) considered that these shifts were masked by the many internal hydroxyls and clay adsorbed water. However, Parfitt and Mortland (1968) indicated that such a shift in the C = O absorption band could be caused by the interaction of carbonyl group and the exchangeable cations. French et al (1954) observed an increase in intensity of the OH stretching band at approximately 3 µ, when the polymer Lytron was adsorbed on H-bentonite and considered it as evidence of H-bonding (Sheppard 1959).

In addition to H-bonding of polymer carboxyl to edge hydroxyl, Emerson (1960) suggested that the hydroxyls of synthetic polymers could be H-bonded to the external or internal planar face silicate oxygens. This type of H-bonding may be possible with the hydroxyls of O.M. Greenland (1956) considered H-bonding as a possible mechanism of adsorption of soil polysaccharides by clays.

Bond between the hydrogen of methylene groups and oxygen of clay surface (CH ... O) has also been proposed on the basis of one dimensional Fourier analysis of diffraction data of montmorillonite-organic complexes (Bradley 1945; MacEwan 1948). However, Laby (1962), Brindley and Hoffmann (1962) observed no lowering of C-H stretching frequencies, which does not support the existence of CH ... O bonds.

II.1.2.3.3. Coulombic interaction

Positive sites at the edges of clay crystals were considered by many workers as responsible for holding negatively charged organic matter and other polymers (Ruehrwein and Ward 1952; Packter 1957; Warkentin and Miller 1958; Mortensen 1962; Emerson 1963). This mechanism is very much pH dependent, the amount adsorbed decreasing with decreasing edge positive charge as the pH is increased.

However, the edge positive charge on montmorillonite is considered very small (de Haan and Bolt 1963; Coleman and Thomas 1967) and may not account for the entire amount of organic matter adsorbed by clays. Ruehrwein and Ward (1952) Warkentin (1956) have reported that the amount of polyelectrolyte adsorbed agreed closely with the number of positive spots on the clay. Schofield (1940, 1949) postulated positive sites on basal plane surfaces of clays due to unbalanced charges within the lattice, caused possibly by an excess of aluminum in the octahedral positions. The possible contribution of such positive spots to adsorption of organic matter is not known. Positively charged amino groups could link to negatively charged clay surface. There is not much evidence of the widespread occurrence of such a mechanism in natural soils, though Swaby (1950) observed that deamination of humates reduced their aggregating effect on soil.

Efficiency of polyvalent cations in promoting adsorption of organic matter and polyelectrolytes was considered to be due to the formation of "bridge linkages."

$$\text{clay}^{-} \ldots M^{n+} \ldots {}^{-}\text{OOCR}$$

(Emerson 1956a, 1963; Evans and Russell 1959; Mortensen 1962; Kononova 1961; Greenland 1965b)

Results of Brydon and Sowden (1959) suggested that Ca bridges are broken by NaCl treatment but not those of Al and Fe. The situation with Al and Fe is more complex than with Ca. Besides the simple Al^{3+} and Fe^{3+} ions, the hydrolysed and polymerised ionic species could also be responsible for such bridges (Greenland 1965b). The exact nature of the link between organic matter and Al^{3+}, Fe^{3+} and their hydroxy species on clay surfaces is still uncertain.

Emerson (1956b), Mortensen (1962), Ahlrichs (1962) expressed the opinion that the carboxyl groups of polyelectrolytes reacted with Al associated with clay surface. It is of interest to note that preadsorption of aurin tricarboxylic acid (aluminon) blocked the adsorption of HPAN on kaolinite which showed that aluminum was involved in one way or another (Mortensen 1962). An attempt to distinguish between crystal edge Al and exchangeable Al was not successful (Ahlrichs 1962).

II.1.2.3.4. Coordination and complex formation

(a) Complexing reactions of organic matter with Al, Fe and their hydroxylated species

Since Bremner et al (1946) reported the occurrence of metallo-organic complexes in soils, a number of workers have obtained evidence supporting their existence (Kononova 1966). Reactions of a podzol B horizon fulvic acid with Al and Fe were studied in detail by Schnitzer and Skinner (1963a, 1963b, 1964, 1965). They reported that Al and Fe were present respectively as $Al(OH)^{++}$ and $Fe(OH)^{++}$ in the complexes with low ratio of Fe or Al to organic matter, and as $Al(OH)_2{}^+$ and $Fe(OH)_2{}^+$ in the complexes with high ratio of Fe or Al to organic matter. Maximum possible molar ratio of metal to fulvic acid was 6, which corresponded to the 6 carboxyl groups present in the fulvic acid they used. The complexes became increasingly water insoluble as the ratio of metal to fulvic acid was increased. Extracting the complexes with different reagents, they found that less Fe than Al was extracted under otherwise identical conditions. This indicates that Fe is held more tightly than Al.

From potentrometric titrations, Schnitzer and Skinner (1963a) inferred that the complexes started to break up at pH 8. Kawaguchi and Kyuma (1959) also observed that humic acid chelates of Fe and Al were partly hydrolysed in a slightly alkaline medium forming hydroxy chelates and completely hydrolysed in strongly alkaline medium. Schnitzer and Skinner (1964) reported that the properties of a metal-organic matter complex extracted from the Bh horizon of a podzol were similar to those of the synthetic complexes with metal to organic matter ratio of 3. However, McKeague (1968) obtained metal to fulvic acid ratios ranging from 3.2 to 12.0 in pyrophosphate extracts of A and B horizons of many soils. This shows that the metal organic matter complexes occurring in nature are much more complex than the synthetic ones prepared by Schnitzer and Skinner (1964). Polyphenols formed during the decomposition of lignaceous material could also complex Al and Fe (Bloomfield 1957; Coulson _et_ _al_ 1960).

Aluminum in organic matter complex exhibits dual nature. A part of it remains capable of exchange while the rest is permanently fixed. In contrast, Fe in humus complexes is not exchangeable to neutral salts (Aleksandrova 1954, 1967). D'Yakonova (1962) reported that tests with NH_4CNS and $K_4Fe(CN)_6$ for ionic iron in humic and fulvic acid complexes were negative. Russell (1963), too, expressed a somewhat similar opinion. He considered that in organic matter complexes, aluminum was present as an exchangeable cation although very strongly bound and iron was present in a chelate.

(b) Coordination and complexing reactions of organic matter with Al, Fe on clay surface

Whether the same kind of complex formation occurs (as discussed earlier) with exchangeable Al, Fe or their hydroxy ions on the clay surface is not definitely known. Even if such reactions are possible, the question arises as to what the nature of linkage of the organic matter-metal complex to the clay surface. These are questions yet to be answered.

Hemwall (1963) explained the adsorption of 4-tert-butyl pyrocatechol on montmorillonite and kaolinite via the formation of a surface aluminum-catechol complex, the aluminum coming from lattice decomposition of the clay. The nature of the complex formed is not known. No report exists on the feasibility of such a reaction between the phenolic groups of organic matter and Al^{3+} ions on clay surface.

I.R. spectroscopic study of adsorption complexes of urea, amides, ketones and benzoic acid has shown direct interaction (or bridged by water molecules) between the carbonyl group and exchangeable metal cations (Mortland 1966; Tahoun and Mortland 1966; Parfitt and Mortland 1968). These authors have interpreted shifts in C = O stretching frequency as indicating the formation of a coordinate bond between the exchangeable cation and the carbonyl group. A bonding of this type may be possible in the case of organic matter.

Chabarek and Martell (1959) considered the hydroxyl ion as a ligand or a complexing agent, and the OH groups attached to Al or Fe atom are generally spoken as co-ordinated hydroxyls. Thus, the compounds formed by the replacement of an OH coordinated to Al or Fe by a carboxyl group could also be considered as a simple coordination compound. Some authors prefer to call such a reaction an exchange one.

Mortensen (1962) observed that adsorbed HPAN (Hydrolysed Poly Acrylo Nitrile) reduced the intensity of O-Al-OH bands at 9.1 u and 10.95 u of kaolinite. This, together with a reduction in the intensity of the band at 2.65 u, led him to suggest that the carboxyl groups in HPAN displaced OH associated with lattice edge aluminum. Bingham et al (1965) considered exchange of acetate ions with exposed structural OH groups as the possible mechanism of acetate retention by montmorillonite. Dosch (1967) observed that the reactions of organic acids and aldehydes with tetracalcium aluminate hydrate was strongly exothermic and postulated the formation of covalent bonds between the inorganic and organic partners. It is of interest to note that the tetracalcium aluminate hydrate is also a layer structured compound with a coherent surface of OH groups.

Leaver and Russell (1957) reported that fulvic acids were effective in blocking sorption of phosphate by soils. They considered that OH groups (attached possibly to Al and Fe) were displaced by carboxylate groups and these OH ions gave rise to a negative surface on the soil particles which repelled phosphate ions. Swenson et al (1949) concluded from studies on phosphate adsorption by Fe, Al and their hydroxides that groups in organic matter could coordinate to Al and Fe to form complexes more stable than basic Al, Fe phosphates. They also found that phosphate adsorbed by $Al(OH)_3$ and $Fe(OH)_3$ was released by organic matter, citrate and tartrate. These reports indicate that the carboxylate groups in organic matter could replace OH bound to Al and Fe in their respective hydroxy compounds. This could be a possible mechanism of retention of organic matter in soils.

According to Aleksandrova and Nad (1958) stable clay-humus complexes were formed through the intermediary of Al, Fe sesquioxides, which make specific bridges between humus substances and clay minerals. The bridges were thought to be "complex aluminum and iron humus compounds with the non silicate forms of sesquioxides and fixed to the surface of the clay minerals by a process of adhesion at the expense of intermolecular types of linkage" (Kononova 1966). Non silicate forms of sesquioxides were thought to be the cross links responsible for the firmness of cementing and adsorption of humus on the surface of clay minerals (Aleksandrova 1967). Electron micrographs of Schulz (1958) indicated that condensation of humic acids in worm casts was promoted by iron oxides. Thus, despite the considerable progress made in the understanding of metal-organic matter complexes, the linkage between soil organic matter and clays is still not clear. It is possible that more than one mechanism is operative depending on the components involved and the environment.

II.2. Al, Fe ionic species in aqueous solutions

An understanding of the nature and properties of the hydrolytic species of Al and Fe is essential to elucidate the possible bonding of O.M. to Al, Fe hydrous oxide coatings on laboratory synthesised Al, Fe hydroxy-montmorillonites.

Both Al^{3+} and Fe^{3+} ions are well known to hydrolyse in aqueous solutions. Formation of the monomeric species in the first instance is generally agreed.

$$Al(6H_2O)^{3+} \rightleftharpoons Al(5H_2O)OH^{2+} + H^+$$

$$Fe(6H_2O)^{3+} \rightleftharpoons Fe(5H_2O)OH^{2+} + H^+$$

II.2.1. Hydroxy aluminum ions

When increasing amounts of base, less than the amount required for complete precipitation of $Al(OH)_3$ is added to an aluminum salt solution, hydrolytic species of the general formula $Al(OH)_x$ $(x < 3)$ are formed. No agreement exists among the workers as to whether the monomeric $Al(OH)^{2+}$ is the dominant (or the only) one or a number of polynuclear hydroxy aluminum ions are formed by further hydrolysis and/or polymerisation.

Hartford (1942), Schofield and Taylor (1954), Frink and Peech (1963b) concluded that the monomeric hydrolysis mechanism accounted for their pH and conductance measurements and the hydrolysis constant calculated thereof. The latter authors also concluded that the Al salt solutions became supersaturated with $Al(OH)_3$ on dilution and remained metastable until the concentration decreased to 10^{-5}M, below which $Al(OH)_3$ was precipitated. Raupach (1963) postulated the formation of $Al(OH)_2^+$ ion also.

Brossett (1952) first postulated the formation of an infinite series of polynuclear complexes with the formula $\left[Al(OH)_3Al\right]_n^{3+}$ and later Brossett _et_ _al_. (1954) amended that the major product could be $\left[Al_6(OH)_{15}\right]^{3+}$ or $\left[Al_8(OH)_{20}\right]^{4+}$ or an infinite series with the formula $\left[Al(OH)_5Al_2\right]_n^{(3+n)+}$. Sillén (1959), in his review article, mentioned the formation of $\left[Al_{13}(OH)_{32}\right]^{7+}$. Matijević and Tezak (1953) initially suggested the formation of a dimer based on colloid coagulation studies, but later (Matijević _et_ _al_. 1961) favoured the existence of an octomer $\left[Al_8(OH)_{20}\right]^{4+}$ in the pH range of 4 to 7. The latter authors observed that the coagulating efficiency of hydrolysed Al solutions was much greater than Al^{3+} solutions. They studied silver halide sols and attributed the above behaviour to the presence of polynuclear species with higher charge.

It was also observed that the hydrolysed Al species reversed the charge on silver halide sols but not Al^{3+} ions.

Ruff and Tyree (1958) studied light scattering by hydrolysed Al solutions and concluded that there exists a distribution of Al atoms among a number of aggregates, the average of which increased with increasing OH/Al molar ratio. Jander and Winkel (1931) demonstrated the existence of higher molecular weight species by measuring diffusion coefficients in basic Al solutions. Rausch and Bale (1964) obtained evidence from X-ray scattering experiments to support the existence of the species $[Al_{13}(OH)_{32}]^{7+}$. Aveston (1965) made ultracentrifugation studies on hydrolysed aluminumperchlorate solutions and interpreted his data as indicating the presence of $[Al_{13}(OH)_{32}]^{7+}$ and $[Al_2(OH)_2]^{4+}$.

Fripiat et al. (1965) suggested the presence of $[Al_4(OH)_8]^{4+}$ based on titrimetric and I.R. absorption data. Hsu and Bates (1964a) poltulated the polymerisation of $Al(OH)_2^+$ ions into 6 membered ring units of composition $Al_6(OH)_{12}^{6+}$ and multiples thereof $[Al_{10}(OH)_{22}^{8+}$ and $Al_{13}(OH)_{30}^{9+}]$. Hsu (1966) dialysed a hydroxy aluminum solution with OH/Al molar ratio of 2.7 and found that about 2/3 of the Al remained in the dialyser bag indicating the presence of a series of polymers. Rich (1960) considered that small hydroxy ions were most likely at low pH and high concentration of Al^{3+} ions. Turner (1968) postulated the formation of polynuclear hydroxy ions to explain potentiometric titration data of Al solutions. Even though the last word on the matter has not been said, it appears that the majority of investigations point to the presence of polynuclear or polymeric hydroxy Al ions in hydrolysed and partially neutralised solutions.

II.2.2. Hydroxy iron ions

The situation with Fe^{3+} ions has been less intensively studied than with Al^{3+}. Lamb and Jacques (1938) reported the "formation of a variety of hydrolysis products but in particular a dilute, nevertheless supersaturated solution of $Fe(OH)_3$" when Fe^{3+} solutions were hydrolysed. Sillén (1959), in his review article, mentioned that the hydrolysis constant varied when measured over a wide concentration range which cannot be accounted for by activity factors or by a second mononuclear species $Fe(OH)_2^+$. He suggested the formation of polynuclear complexes with the formula $[Fe_x(OH)_y]^{(3x-y)+}$. This was further supported by spectrophotometric and magnetic measurements. Siddall and Vosburgh (1951) and Milburn and Vosburgh (1955) concluded from spectrophotometric measurements that polynuclear hydrolytic species, possibly $\left[Fe(OH)_2Fe\right]^{4+}$, was present in solutions more concentrated than 10^{-3}M. Gimblett (1963), while conceding to the formation of polynuclear hydroxy ferric ions, pointed out that the tendency to form polynuclear hydrolytic species was greater for aluminum than iron. A condensed review and discussion of the polynuclear hydrolytic species of Al and Fe has been given by Gimblett (1963).

There is a great deal of evidence to the presence of polynuclear and polymeric species of hydroxy Al and Fe ions, even though the controversies are not fully settled. The situation in solutions more dilute than 10^{-3}M (Milburn and Vosburgh 1955) could be different as was pointed out by Frink and Sawhney (1967), but not much is known of the species in very dilute solutions.

II.3. Hydroxy Al, Fe ions (positively charged hydrous oxides) on clay surfaces

Properties of clays with natural and synthetic coatings (inter layers) of positively charged Al and Fe hydroxy compounds have been studied by many workers in the last fifteen to twenty years (Brown 1953; Rich and Obenshain

1955; Rich 1960, 1968; Shen and Rich 1962; Dixon and Jackson 1962; Jackson 1963; Barnhisel and Rich 1963; Coleman et al. 1964; Hsu and Bates 1964b; Clark 1964; Frink 1965; Thomas and Swoboda 1963; Turner and Brydon 1965; Turner 1965, 1967). These coatings occur on both internal and external surfaces of clay minerals and were considered to be one of the major contributors for pH dependent charge of soils. Positively charged Al and Fe hydroxy compounds were considered not exchangeable to neutral unbuffered salt solutions and firmly held to clay surfaces (Coleman and Thomas 1967). An extensive review on the conditions of formation and properties of hydroxy interlayers has been given by Rich (1968).

The question of whether the hydroxy aluminum compounds deposited on clay surfaces under laboratory conditions are present as a continuous solid phase or are adsorbed as hydroxy aluminum polymers is not well settled. Frink and Peech (1963a) considered that the non-exchangeable aluminum was present as $Al(OH)_3$, but their data indicated that the non-exchangeable Al had a charge of 0.64 to 0.38 equivalents per mole of Al, the origin of which was not explained. Shen and Rich (1962) reported that "fixed" Al in montmorillonite was present as $Al(OH)_2^+$ for initial OH/Al molar ratios up to 1.35. Schofield (1946) proposed a polymeric chain structure for the non-exchangeable Al. Turner (1965) calculated the charge on "fixed" aluminum on montmorillonite from the decrease in C.E.C. caused by precipitated Al and reported that the "fixed" hydroxy Al had a formula equivalent to $Al(OH)_{2.7}^{0.3+}$, when the initial OH/Al molar ratio ranged from 1 to 2.7. Hsu and Bates (1964b) reported that in the case of vermiculite the fixed Al was present as ring units with formula $Al_6(OH)_{12}^{6+}$ or $Al_{10}(OH)_{22}^{8+}$, when the initial OH/Al molar ratio ranged from 0.3 to 2.1 and that the polymers increased in size and the net positive charge per Al atom decreased as the OH/Al ratio was increased to less than 3. Sawhney (1968) obtained an average charge of 1 me/Al atom for OH/Al = 2 and 0.5 me/Al for OH/Al = 2.4 for montmorillonite and vermiculite. When the clays were aged for 10 weeks in hydroxy aluminum solutions, the charge was reduced to 0.2-0.3 me/Al atom. C.E.C. reductions (blocking of permanent charges) of clay by the addition of hydroxy aluminum compounds up to an initial OH/Al molar ratio of 3 have been reported (Rich 1960; Shen and Rich 1962; Barnhisel and Rich 1963; Hsu and Bates 1964b; Turner 1965; de Villiers and Jackson 1967).

In the case of iron hydrous oxides, even though interlayering (Rich 1968; Herrera and Peech 1968) and

C.E.C. reductions (blocking of permanent charges) of clays (Coleman _et_ _al_. 1964; Clark and Nichol 1968) have been observed, the effect has been very temporary. Clay-iron hydrous oxide complexes were reported to be unstable above pH 3 (Clark and Nichol 1968), the hydrous oxide undergoing further hydrolysis and forming $Fe(OH)_3$.

Slaughter and Milne (1960) considered that the Al-hydroxy compounds were adsorbed initially over the entire surface (i.e., both internal and external surfaces), rather than the direct formation of a structure in the interlayer. On the other hand Brydon and Kodama (1966) interpreted from I.R. absorption and D.T.A. curves that the "aluminum hydroxide" entered entirely into the interlayer of montmorillonite and assumed a gibbsite-like monolayer structure up to 8 me of added Al/g clay. When the amount was higher than this but below the amount (16 me Al/g) required for a perfect gibbsite layer, some hydroxide was present external to the interlayer space. The reason for this behaviour was not known. Electron micrographs of hydroxy aluminum polymer treated (15 me Al/g) vermiculite showed the presence of hydrous oxide on external surfaces (de Villiers and Jackson 1967). Treatment of clays with hydroxy aluminum solutions reduced the C.E.C. to practically zero (Rich 1960; Barnhisel and Rich 1963) which indicates that the hydroxy

Al compounds were deposited on both internal and external surfaces. Dixon and Jackson (1962) considered that the interlayers existed as islands more concentrated around the edges of clay plates. Frink (1965) also concluded that interlayers in natural soils occurred as clusters of islands or "atolls."

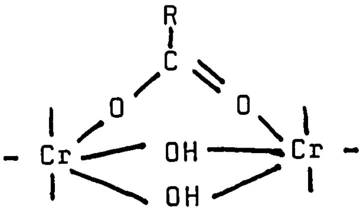
II.4. Anion penetration

A number of reports have been made that the pH increased on the addition of anions both inorganic and organic to solutions of basic chromium, iron, aluminum and zirconium solutions and their hydroxides (Bailar 1956). This phenomenon has been explained by postulating anion penetration. Anion penetration refers to "the competition between hydroxyl ions and other anions for positions in the first coordination sphere of a metal ion and the related displacement of coordinated groups such as aquo, hydroxo or an anion by another anion" (Bailar 1956; Gimblett 1963). The increase in pH referred to earlier has been attributed to the replacement of coordinated OH ions and release into solution. Anion penetration in olated complexes was found to be controlled by the relative coordinating tendencies of the entering anion and the group which it displaces, the relative concentrations of the reactants, the length of time for which the solutions were allowed to react, and the conformation in the case of organic anions (Bailar 1956; Gimblett 1963).

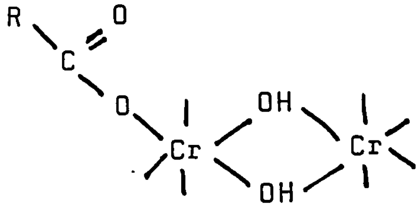
Displacement of OH ions from the hydroxy compounds involves coordination of the displacing group to the metal ion. Reactivity of organic anions (in anion penetration) is therefore determined partly by the number of donor groups and their relative positions in the anion. Thomas and Whitehead (1931) and Thomas and Vartanian (1935) observed increase in pH of aluminum hydrosol when organic anions were added and explained it on the basis of anion penetration. Thomas and Kremer (1935) compared the effectiveness of aliphatic monocarboxylate anions from formate to valerate and dicarboxylate anions from oxalate to pimelate, in anion penetration. Difference between the homologous monocarboxylate anions was only very slight. This was as expected since coordination of these anions with the metal ion would be controlled by the single carboxyl group. With the dicarboxylate anions the effectiveness was pimelate ⩽ adipate ⩽ glutarate < succinate < malonate < oxalate. This was explained as due to the formation of chelate rings. Carboxyls in glutarate and higher homologues were so far apart that the anions behaved like monocarboxylates. In the lower homologues, where the carboxyls are closer, the anions were more reactive possibly due to the formation of 5 or 6 membered rings which are more stable than the larger ones. Importance of conformation was demonstrated by using the cis-trans isomers, malate and fumarate. Malate was found to be more effective than fumarate possibly because of chelation (Bailar 1956). An excellent review of the work of Thomas and co-workers has been given by Pokras (1956). Thus it appears that chelation is a factor that promotes anion penetration.

Kubelka (1949) reported that pyrogallol expelled sulphate in basic chromium complexes but resorcinol or hydroquinone did not.

Two types of structures have been proposed for the complexes formed when an organic anion displaced an OH group from an olated chromium complex (Bailar 1956).



I



II

Even though the effects of anion penetration have been observed, the exact structure (in the case of organic anion complexes) is not well elucidated.

II.4.1. Anion penetration in hydrous oxide-clay systems

The concept of anion penetration is not entirely new to soil science. Mattson (1931) and Mattson and Wicklander (1940) observed that Cl^- and SO_4^{2-} were held in quantity only by soils which had large amounts of Al, Fe hydrous oxides. They considered that these anions were in competition with OH ions found in hydrous oxides. Liu and Thomas (1961) and Chang and Thomas (1963) assumed that the sulphate ions were held by the Al, Fe hydrous oxides on clay surfaces according to the reaction

$$SO_4^{2-} + R_x(OH)_y - \text{clay} \rightarrow R_x\left[(OH)_{y-2}(SO_4)_2\right] - \text{clay} + OH^-$$

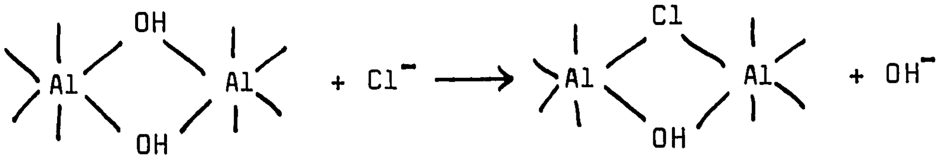
where

$R = Al$ or Fe

Edwards et al. (1965) observed 7.5 me/100 g of positively adsorbed Cl^- ions in Al-montmorillonite and proposed that Cl^- ions reacted with $Al(OH)_2^+$ on the clay surface to form $Al(OHCl)^+$.

$$Al(OH)_2^+ - \text{clay} + Cl^- \rightarrow Al(OHCl)^+ - \text{clay} + OH^-$$

Similarly de Villiers and Jackson (1967) explained the abnormal increase in Cl^- retention by partially chloritized vermiculite, when the pH was increased from 4 to 5 as due to anion penetration.



Iron hydroxide was observed to adsorb anions such as Cl^- and SO_4^{2-} in larger quantities than an equivalent weight of aluminum hydroxide (Thomas and Swoboda 1963). Jurinak (1966) mentioned the anion penetration of SO_4^{2-} and HPO_4^- on hematite. Hingston et al (1968) considered that the retention of selenite and phosphate ions by goethite was according to the following reaction:

$$\text{Surface} - OH + SeO_3^{--} \rightleftharpoons \text{Surface} - SeO_3^- + OH^-.$$

They described that these ions were octahedrally coordinated with Fe^{3+}, which, in other words, is a case of anion penetration. De Villiers and Jackson (1967) considered the anion penetration by acetate ions (in exchange for OH ions) in olated hydroxy aluminum complexes formed on clay surfaces.

Schwertmann (1966) observed that no crystalline goethite was formed when amorphous ferric hydroxide solutions were boiled with strong alkalis in the presence of organic matter. It was also noted that goethite readily formed under otherwise identical conditions in the absence of organic matter. He attributed this phenomenon to some sort of anion adsorption (of organic matter) by ferric hydroxide. Schwertmann et al later reported similar observation with citrate anions and suggested a reaction of the following type, where the anion becomes a coordinator of the surface Fe atom:

$$— \mathrm{Fe_x(OH)_{m,n}} + \mathrm{m(Citr)^{n-}} \rightleftharpoons - \mathrm{Fe_x(Citr)_m} + \mathrm{m.n\ OH^-}$$

It is to be noted that in anion penetration, it is not necessary that the whole anion (in the case of complex anions) should enter into the hydroxo-complex. This may happen in the case of small anions like Cl^- but in the case of anions like SO_4^{2-}, $H_2PO_4^-$ and the organic anions, it is essentially the oxygen of the anion and not the whole anion which occupies the coordination position around the metal ion.

II.5. Summary

Soil organic matter is a heterogeneous system of polymers and has functional groups capable of reacting with Al, Fe, their hydroxy ions and hydroxides. Simple electrostatic interaction, coordination and chelation are operative in these reactions. Adsorption of organic matter on clays is influenced by pH, nature of exchangeable cations and presence of Al, Fe hydrous oxides on clay surfaces. A great deal of information on adsorption mechanisms has been gathered from the study of adsorption of simple organic compounds and synthetic polyelectrolytes on clays.

While edge face and planar face associations of organic matter and polyelectrolytes with clays have been postulated, there is no general agreement on the interlamellar adsorption of humus substances by montmorillonite. Physical adsorption, coulombic interaction, hydrogen bonding, coordination and complex formation have been considered as possible mechanisms of interaction of organic matter with clays. Anion penetration is also a pH dependent mechanism and from a review of the available literature it appears that the replacement of hydroxyl groups attached to Al, Fe hydroxy compounds by carboxyl groups in organic matter could be a possible mechanism of interaction of organic matter with the mineral constituents. Since organic matter has been shown to possess ability to chelate Al, Fe, the possibility of such a mechanism would be enhanced. No single mechanism is sufficient to explain the observed adsorption characteristics and it is possible that more than one mechanism is operative at one and the same time.

It therefore seems that an investigation of the (1) adsorption and retention characteristics,

(2) sites of adsorption

(3) possible mechanisms of bonding of organic matter on hydrous-oxide coated clay (laboratory synthesised) would contribute towards the understanding of the organo-mineral complex in soils.

III. MATERIALS AND METHODS

III.1. Montmorillonite Clay

The source of Montmorillonite was Wyoming bentonite (Na-clay) obtained from American Colloid Corporation, Chicago, U.S.A. Less than 2 μ clay fraction was separated by dispersion and sedimentation (Day 1965). A stock solution of approximately 1.5% clay was prepared.

III.2. Organic Matter

Two organic matter preparations were used in the study. Preparation I, hereafter referred to as O.M.I (organic matter I) was extracted from a peat with 0.5 N NaOH under N_2 gas, after pretreatment with 0.1 N HCl (Levesque and Schnitzer 1965; Mortensen 1965). The peat sample was collected at a depth of 15-24 inches from a pit in the Macdonald College farm. When freshly collected, the sample was very wet and had a black to very dark brown (10 YR 2/1-2/2) colour. The material turned darker (10 YR 2/1) and very hard on air drying. Air dry material was ground to pass a 2 mm sieve before extraction.

Preparation II, hereafter referred to as O.M.II (organic matter II), was extracted the same way, from the L-H layer material under hemlock trees, collected in the Morgan Arboretum, Macdonald College. Extraction of O.M. with NaOH was done twice on 10 g sample using 100 ml of extractant, with overnight shaking. Supernatant liquid was centrifuged and filtered. The extract was diluted to give approximately 0.3% organic matter suspension. The O.M. suspensions thus prepared were passed twice through Amberlite IR-120 exchange resin in the H-form and stored under a thin layer of toluene.

III.3. Clay Preparations

(a) Hydroxy Al, Fe solutions

Hydroxy Al and Fe solutions (polymeric) were prepared by adding calculated amounts of 0.1 N NaOH to 1 N $AlCl_3$ or 1 N $FeCl_3$ solution with constant stirring at the rate of about 50 ml in 30 mins (Hsu and Bates 1964a; de Villiers and Jackson 1967) to give OH to Al or Fe molar ratios of 2.5 and 2.7. The final hydroxy solution was diluted with distilled water to contain 0.02 eq Al or Fe per litre, and stirred for 1 hour. Hydroxy polymer solutions were prepared afresh before use.

(b) Hydroxy Al, Fe coated clays

Aliquots of stock Na-clay were passed through a Dowex-50 exchange resin column in the H-form and the H-clay (strictly H-Al clay) obtained was neutralised with NaOH to the pH of respective hydroxy polymeric solutions, allowed to stand for 1 hour, and the pH then rechecked and adjusted if necessary. Supernatant liquid was removed by centrifugation and decantation. Hydroxy polymer solutions were added to the clay at the rate of 15 me Al or Fe/g clay in centrifuge bottles and shaken continuously for two weeks (Rich 1960; de Villiers and Jackson 1967). The hydroxy polymer solution was added in two instalments, one-half initially and the other half at the end of 1 week, after centrifuging and removing the spent solution. At the end of 2 weeks, the clays were centrifuged and washed free of chloride with distilled water. Hydroxy Al or Fe coated clays were prepared afresh before use in each experiment. X-ray diffraction patterns and electron micrographs were obtained on these preparations.

(c) Al, Fe and Na saturated clays

Al, Fe saturated clays were prepared by neutralising the H-clay to the pH of 1 N $AlCl_3$ (pH 3.04) or 1 N $FeCl_3$ (pH 2.62) solution, removing the supernatant by centrifuging and then washing the clays 5 times (at the rate of 50 ml/g clay) with 1 N $AlCl_3$ or 1 N $FeCl_3$ solution. Clays were then washed free of Cl^- with ethyl alcohol. Na-saturated clay was prepared by washing the original clay ($<2\mu$) 5 times with 1 N NaCl as described above and finally washing the clay free of Cl^- with ethyl alcohol. Weight per unit volume of the differently treated clays and the per cent increase in weight of the Al or Fe polymer solution treated clays were determined.

III.4. Chemical Analysis

(a) pH and conductivity

pH measurements were made with a Sargent Model DR pH meter using a Sargent S-30072-15 glass-calomel combination electrode. Conductivity was measured using a Radiometer conductivity meter using a dip type (CDC 114) Radiometer conductivity cell.

(b) Organic carbon

Organic carbon in solution was determined by the dichromate-sulphuric acid colorimetric method (Carolan 1948). Two ml aliquots containing less than 0.5 mg O.M. were pipetted into colorimeter tubes, 5 ml dichromate-sulphuric acid solution added, and allowed to stand for

30 mins. Transmittance was determined against a blank containing 2 ml distilled water and 5 ml dichromate-sulphuric acid solution using a red (660 mμ) filter on an Evelyn photoelectric colorimeter. Sucrose standards were used for calibration.

(c) Al

Aluminum was determined by the Eriochrome Cyanine-R colorimetric method (Jones and Thurman 1957). The method was modified to suit determination on a Technicon Auto Analyser, the flow diagram for which is given in Appendix Figure 1. Hydroxy-aluminum solutions were depolymerised by boiling with 0.1 N HCl before Al determination. Iron compensating solution and thioglycollate were omitted in cases where it was definitely known that Fe was not present.

(d) Fe

Iron was determined by the O-phenanthroline colorimetric method (Olsen 1965) on a Technicon Auto Analyser (Methodology I.1.d), the flow diagram for which is given in Appendix Figure 2. Hydroxy iron solutions were depolymerised by boiling with 0.1 N HCl before Fe determination.

(e) K

Potassium determinations were done flame photometrically on a Technicon Auto Analyser.

III.4.1. Organic matter extract

(a) Conductometric and potentiometric titrations

Conductometric titrations were carried out on 30 ml aliquots of acid O.M. extracts under N_2 gas using N/30 $Ba(OH)_2$ and N/30 NaOH. Potentiometric (pH) titrations were also done on 30 ml aliquots under N_2 gas using N/30 NaOH.

(b) Organic matter and ash content

Organic matter content in the extract was determined by evaporating 10 ml aliquots in crucibles at 100°C in an oven and determining the weight of residue. Ash content was determined by heating the above residue overnight at 600°C in a muffle furnace (Schnitzer *et al*. 1959).

(c) Total N

Total N in the O.M. extract was determined by the semi-micro Kjeldahl procedure (Bremner 1965) using 10 ml aliquots.

(d) Total Al, Fe

Ten ml of O.M. extract was digested with H_2SO_4-H_2O_2 mixture (Lindner and Harley 1942) and Al, Fe in the digest was determined respectively by the Eriochrome Cyanine-R and O-phenanthroline colorimetric methods as described in section III.4.

(e) Total acidity

Total acidity (COOH + phenolic OH) of the O.M. extracts was determined by baryta absorption under nitrogen (Brooks and Sternhell 1957; Kononova 1966). Ten ml of the acid O.M. extract was shaken overnight with 50 ml of N/30 $Ba(OH)_2$ and the unreacted $Ba(OH)_2$ was determined by the titration of aliquots of supernatant solution with N/30 HCl using phenolphthalein as indicator.

(f) Carboxyl groups

Carboxyl groups were determined by the calcium acetate method (Brooks and Sternhell 1957; Kononova 1966). Ten ml of acid O.M. extract was treated with 50 ml of 0.5 N calcium acetate in a 250 ml volumetric flask and allowed to stand for 4 days with occasional shaking (Kononova 1966). Solution was made up to volume and the liberated acetic acid was determined by titrating aliquots with N/30 NaOH using phenolphthalein as indicator. A blank titration on calcium acetate similarly diluted was made and the necessary corrections made.

(g) Per cent humic acid

Ten ml aliquots of O.M. extracts in previously weighed glass centrifuge tubes were acidified to pH 1.0 with conc. HCl (Stevenson 1965), centrifuged washed once with distilled water, dried at 100^{o}C and weighed.

III.4.2 Clays

(a) Exchangeable Al, Fe ions

Ions (Al, Fe) exchangeable to 1 N KCl on the respective hydroxy-clays were determined by methods described in section III.4.

(b) C.E.C. (Cation Exchange Capacity)

C.E.C. of the clay preparations (effective permanent charge) was determined using unbuffered 1 N KCl as saturating solution and 1 N NH_4OAc as the displacing solution (Jackson 1960). C.E.C. of the original bentonite clay was also determined at the respective pH value (pH 4.6 and pH 5.3) of the Al hydroxy-clay preparations and at pH 7 using buffered KOAc for saturation and NH_4OAc for displacement. The Na-clay was repeatedly equilibrated with buffered KOAc until the pH of the supernatant was the same as that of the saturating solution (de Villiers and Jackson 1967). Potassium was determined flame photometrically.

(c) "Fixed" Al on hydroxy Al treated clays

"Fixed" aluminum was determined by extracting aliquots of clay suspension containing approximately 0.1 g clay, five times each with 5 ml of 0.2 N HCl (Shen and Rich 1962; Sawhney 1968). A similar control extraction was done on Na-bentonite and the amount of structural Al removed was deducted from the above determination. Exchangeable Al was also deducted from the above value to obtain "fixed" Al.

(d) Total iron

Total iron in the hydroxy iron solution treated clays was extracted by the citrate-dithionite procedure (Jackson 1960) and determined with O-phenanthroline as described previously.

III.5. X-ray Diffraction

X-ray diffraction patterns of clay preparations and clay organic matter complexes were obtained with a North American Philips' Geiger Counter X-ray spectrometer Type

12021 using Cu Kα radiation. Oriented specimens on glass slides were used (Whittig 1965). Specimens on the slides were heated in an oven at 100°C or 200°C as and when required and the X-ray diffraction tracing recorded immediately after removing the specimens from the oven.

III.6. Electron Micrographs

Suspensions of clay preparations and clay-organic matter complexes containing 1-5 mg/ml were prepared by suitable dilution and dried on formvar coated grids. The specimens were shadowed in a Balzer's 510 M shadow caster at 30-40° with platinum wire on tapered carbon electrodes. Preparations were examined and photographed using an A.E.I. E.M.6B electron microscope, the microscope magnification being 20 to 30 thousand.

III.7. Infra-red Absorption Spectrum

Organic matter preparations, clay specimens, and organic matter-clay complexes were freeze-dried for 48 hours and then further dried over P_2O_5 for two days before the spectra were recorded. Spectra were taken on KBr discs (Schnitzer 1965). 0.5 to 1 mg (double the weight in the case of clay-O.M. complexes) of the dried sample was ground for 2 mins with 400 mg of previously dried KBr in a mortar and then transferred into a KBr disc press, which was subsequently evacuated. Discs were pressed at 20 tons pressure for 15 mins and the spectra recorded on a Perkin-Elmer Model 257 grating infra-red spectrometer from 4000 cm^{-1} to 625 cm^{-1}. Check runs with KBr alone were also made to ensure the dryness of the KBr used. Exact positions of the peaks were determined by comparison with the peaks of standard polystyrene film.

III.8. Experiments

III.8.1. Adsorption studies

Experiment I

Five ml aliquots of acid O.M.I and O.M.II suspensions were added separately to 5 ml aliquots of the different clay preparations in 50 ml weighed centrifuge tubes and shaken continuously for 2 weeks in a shaker. At the end of 2 weeks, the suspension was centrifuged (at 3000 r.p.m.) and the pH of and organic carbon in the supernatant determined as described earlier in section III.4. The centrifuge tube with the residue was weighed and the amount of unadsorbed organic carbon present in the residue calculated. Residue in the centrifuge tube was washed repeatedly with 5 ml aliquots of distilled water using the centrifuge, until the supernatant liquid was colourless. Usually 6-7 washings were sufficient. Collected supernatant was made up to 50 ml volume and the organic carbon concentration determined.

The residue in the centrifuge tube was shaken for 5 mins with 5 ml of 0.5 N Na_2CO_3 solution, centrifuged and the supernatant collected. The process was repeated until no more organic matter was extracted. Usually 8-9 washings were sufficient. As the number of extractions increased, the suspension became more dispersed and higher speeds coupled with longer time of centrifugation had to be used to obtain clear supernatant liquid. Organic carbon concentration in the combined washings was determined. Residue in the centrifuge tube was similarly extracted with 5 ml portions of 0.5 N NaOH and the organic carbon concentration in the combined washings was determined.

The amount of free organic carbon (unadsorbed) carried in the residue was subtracted from the amount extracted by water. Total amount of organic carbon adsorbed was calculated from the difference between the amount added and the amount remaining unadsorbed. Amounts of organic carbon desorbed by the different extractants were also calculated. A second set of determinations was carried out exactly the same way with previously neutralised (with NaOH) to pH 7 O.M. suspensions. Organic carbon values were converted to organic matter.

Experiment II

Added separately, aliquots of O.M.I and O.M.II suspensions ranging from 0.5 ml to 6 ml to 2 or 3 ml aliquots (containing approximately 0.04 g clay) of the different clay preparations in 50 ml centrifuge tubes. Adjusted the pH with NaOH to the corresponding pH of the clay preparations, made up the volume to 10 ml, allowed to stand for 1 hour, then rechecked the pH and adjusted if necessary. Suspensions were shaken continuously for 2 weeks on a shaker. At the end of 2 weeks, the suspensions were centrifuged (at 3000 r.p.m.) and the concentration of the unreacted organic carbon in the supernatant was determined. Amount adsorbed was calculated by difference as in the earlier experiment. A second set of determinations was carried out exactly the same way except that the pH of the organic matter-clay mixture was adjusted to pH 7 with NaOH before equilibration. Organic carbon values were converted to organic matter.

Experiment III

Five ml of the differently prepared hydroxy-clay suspensions were added separately to 5 ml of acid O.M.I suspension in 50 ml centrifuge tubes and shaken continuously for 2 weeks. At the end of 2 weeks, suspensions were centrifuged, washed free of unadsorbed organic matter with distilled water. X-ray diffraction tracings of the air dry, glycerol solvated, "heated at 100°C for 6 hrs," "heated at 200°C for 24 hrs," clay-organic matter complexes, were obtained. Temperature higher than 200°C was not used because the O.M. started to oxidize above 200°C. Electron micrographs of the clay-organic matter complexes were obtained 2 weeks after preparation of the complexes. A second series was carried out the same way with O.M.I suspension neutralised to pH 7 with NaOH. Control treatments with clay only were included for comparison.

III.8.2. Reactions of organic matter with Al, Fe hydroxy compounds in solution

Experiment IV

The technique of Thomas and Whitehead (1931) was used to study the possibility of a reaction of O.M. of the "anion penetration" type, with hydroxy Al, Fe compounds. Added in separate 40 ml glass tubes, 5 ml of O.M. suspensions previously neutralised to pH 7 or to pH values of the corresponding hydroxy polymeric solutions and 5 ml of Al or Fe hydroxy polymer solutions. In two treatments, the respective hydroxides precipitated at pH 7 and freed of supernatant solution were used. A few drops of toluene were added to the tubes to minimize microbial activity (Myers 1937; Kononova _et_ _al_. 1964). Contents were mixed well and allowed to stand. pH was measured at the end of 3 hours, 1 day and 1 week. Several model organic compounds (0.1 N solution of organic acids and polyphenols, Table 8 section IV.3.1) neutralised to pH 7 with NaOH were also included in the experiment. pH values of the mixtures of solutions of these model compounds and the Al or Fe hydroxy polymer solutions were measured under similar conditions. Treatments designed to determine the relative effect of possible hydrolysis of the organic salts and neutralised O.M. under above conditions, were also included in the experiment.

Experiment V

One ml of acid O.M.I suspension was added in two sets to a series of 125 ml Erlenmeyer flasks containing 10 ml Al hydroxy polymer solution with OH/Al molar ratio 2.5. Graded amounts of 0.1 N NaOH ranging from 0.05 ml to 4 ml were added to give a final range of pH from 4 to 11. The solutions were mixed well and allowed to stand for 1 day. Equilibrium pH of the solutions was measured the next day. Forty ml of distilled water was added to one set of flasks and the acidity or alkalinity was determined by titration with N/30 NaOH or N/30 HCl using phenolphthalein as indicator.

Total OH (free + bound) was determined by reacting the suspensions with KF (Hsu and Bates 1964a; McLean 1965). Forty ml of 1 N KF solution was added to the second set of flasks and the OH liberated was titrated with N/30 HCl using phenolphthalein as indicator. Flasks were then heated for 2 hrs at 90°C on a water bath and again titrated with HCl. This heat and titration procedure was repeated until the pink colour developed after heating was only faint (Hsu and Bates 1964a). A blank containing KF and O.M.I extract was similarly treated and the necessary corrections were made. A second set of determinations exactly the same as the above was carried with the Al hydroxy solution alone (i.e., no O.M. added).

The amount of OH bound to Al at different pH values was calculated from the values of total OH and free OH or free acidity. Al in the Al hydroxy polymer solution was determined as described earlier in section III.4, after depolymerisation by boiling with HCl. The OH/Al ratio was calculated at the different pH values. Amounts greater than 1 ml O.M.I could not be used due to difficulty in detecting the end point. The method was unsuccessful when applied to the hydroxy Fe system due to difficulty in detecting the end point.

Experiment VI

Twenty ml aliquots of O.M. extracts were taken in 100 ml centrifuge tubes and 30 ml of Al or Fe hydroxy polymer solution or Al^{3+} or Fe^{3+} (in equivalent concentration) solution was added and the pH adjusted with NaOH to the pH of the respective Al or Fe solution. The mixture was allowed to react, for 2 weeks with constant shaking. A separate set was similarly treated with O.M. extracts neutralised to pH 7. Ratio of O.M. to Al or Fe was approximately 1 equivalent O.M. (COOH) to 4 equivalents of Al or Fe. Excess Al or Fe solution was used to ensure maximum possible reaction of the O.M. At the end of 2 weeks, the suspensions were dialysed free of chloride against distilled water and then freeze dried. Control treatments of O.M. with pH similarly adjusted and treatments using tartaric acid (in place of O.M.) were also included for comparison purposes. I.R. spectra of the complexes were recorded as described earlier (section III.7).

III.8.3. Reactions of O.M. with hydroxy Al, Fe compounds on clay surface

Experiment VII

Five ml aliquots of hydroxy Al or hydroxy Fe solution treated clay were pipetted into 40 ml glass tubes, centrifuged and the clear supernatant liquid decanted. Added 10 ml of O.M. suspensions previously adjusted to pH 7 or to pH of the corresponding clay preparation and a few drops of toluene, mixed well and allowed to stand. pH of the supernatant was determined after 3 hrs, 1 day and 1 week as in experiment IV.

Experiment VIII

Five ml aliquots of the different hydroxy clay preparations were added separately to 5 ml of O.M.I extract and the pH adjusted to the pH of the corresponding clay suspension. The mixture was shaken continuously for 2 weeks. Suspension was centrifuged (3000 r.p.m.), washed with distilled water to remove unadsorbed organic matter, freeze dried and the I.R. spectra of the clay-O.M. complex was recorded.

III.8.4. Effect of O.M. on the formation of X-ray crystalline $Al(OH)_3$

Experiment IX

Separate 10 ml aliquots of Al hydroxy polymer solution with OH/Al molar ratio of 2.5 was added to 10, 5, 3.3 and 2 ml of acid O.M.I suspension contained in 50 ml centrifuge tubes and allowed to stand for 1 week with occasional shaking. A control with no O.M. was also included. The mixtures were adjusted to pH 8 with NaOH and allowed to stand for 2 weeks with occasional shaking. They were then dialysed free of Cl^- against distilled water. The precipitates were centrifuged, washed and X-ray diffraction tracings were obtained; immediately after dialysis, 1 month after and 3 months afterwards.

Experiment X

Specimens from experiment III were aged for 3 months and X-ray diffraction tracings and electron micrographs were taken.

III.9. General

All determinations were done in duplicate. All experiments and analyses were carried out at room temperature (25°C) unless otherwise specified. Chemicals used were all Fisher certified A.C.S. chemicals. All results are expressed on an oven dry basis per 100 g clay.

IV. RESULTS AND DISCUSSION

IV.1. Characterisation of materials used

IV.1.1. Organic matter

The physico-chemical characteristics of the two O.M. extracts used in this study were somewhat similar except for the functional groups content and the pK value (Table 1). Apparent pK value was obtained from the potentiometric titration curve (Figure 1), at 50% neutralisation, using the Henderson-Hasselbalch equation,

$$pH = pK + n \log \left(\frac{\alpha}{1-\alpha}\right)$$

where α is the degree of neutralisation, K the apparent dissociation constant of the acid and n an empirical constant. Complete neutralisation was arbitrarily chosen at pH 8.0 (Martin and Reeve 1958; Khanna and Stevenson 1962). No correction was made for ionic strength. The apparent pK values of 4.6 and 5.5 respectively for O.M.I and O.M.II were well within the range of values reported in the literature for O.M. preparations (Khanna and Stevenson 1962). Since both the O.M. preparations contained nearly equal amounts of both Al and Fe (Table 1), the higher pK

TABLE 1. Chemical characteristics of organic matter preparations

	O.M.I	O.M.II
pH	2.86	3.05
Concentration (O.M.) mg/ml	2.73	2.81
Organic carbon mg/ml	1.37	1.39
Humic acid %	64.9	74.5
Ash %	2.45	4.70
pK	4.6	5.5
Total Al me %	65	69
Total Fe me %	4	6
N %	2.93	2.37
Total acidity me %	577	505
Carboxyl me %	254	213
Phenolic hydroxyl me %	323	292

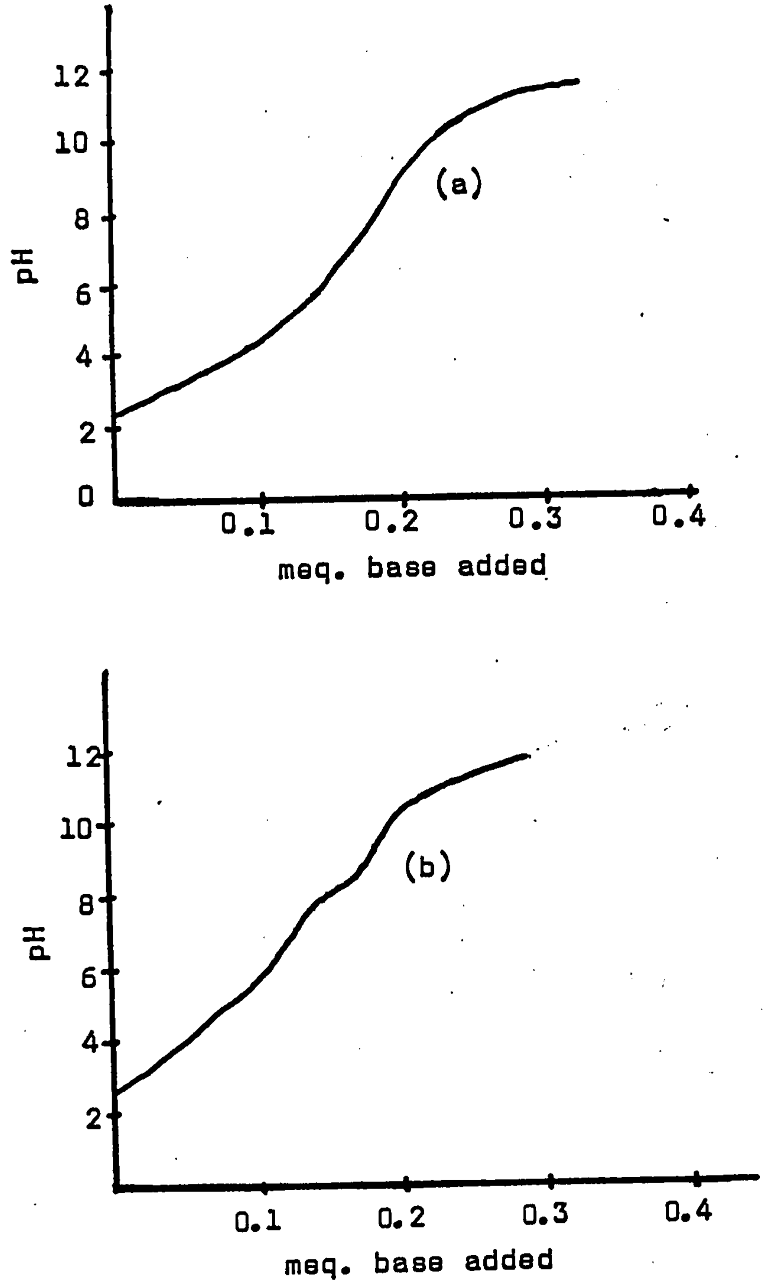


Figure 1. Potentiometric titration curves of O.M. preparations.
(a) O.M.I; (b) O.M.II

value of O.M.II was due to the weaker acid nature (on the average) of its carboxyl groups than the carboxyls of O.M.I. This was in agreement with the observed pH of the O.M. suspensions (Table 1). Phenolic hydroxyl was obtained (Table 1) from the difference of total acidity and carboxyl content.

Conductometric titration curves (Figure 2) indicated the presence of complexing or chelating groups in the O.M. preparations. Difference in shape of the conductometric titration curve (Figure 2) when $Ba(OH)_2$ and NaOH were used separately as titrant was interpreted as for chelating carboxylic acids like E.D.T.A. (Chaberek and Martell 1959). The level portions of the curves were possibly due to complex or chelate formation between Ba and O.M., where both Ba and OH ions disappeared from the solution. Since a reaction of this type would have involved the replacement of the large anion (O.M. ligand) by a second anion of almost the same size (Ba-complex or chelate) little change in conductivity was observed. A similar interpretation of the conductometric titration curve of an O.M. preparation was made by Schnitzer and Skinner (1963). Presence of carboxyl groups of different strength was indicated by the number of inflexion points on the curve (Figure 2). O.M.I showed a small, second level portion on the curve at a

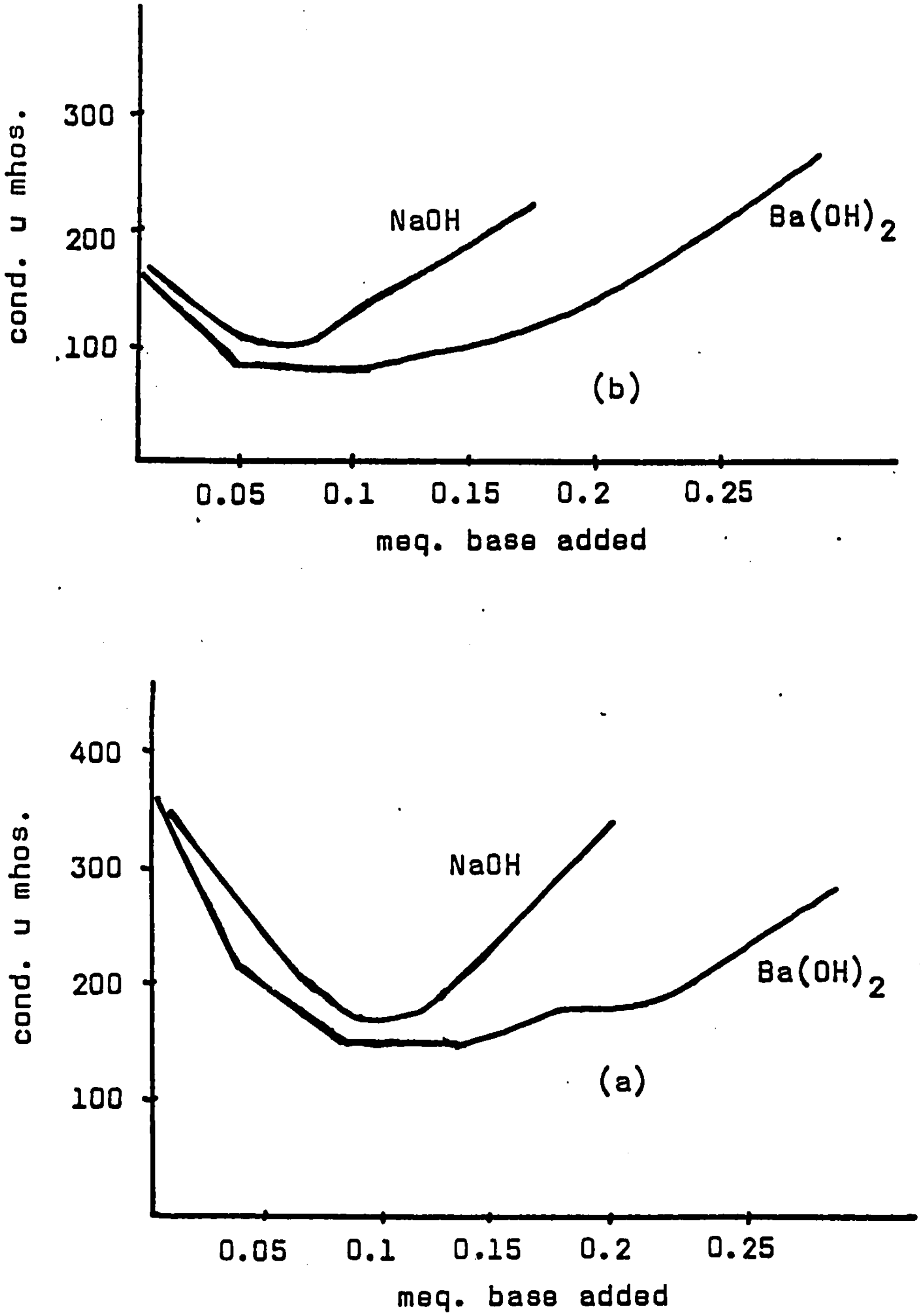
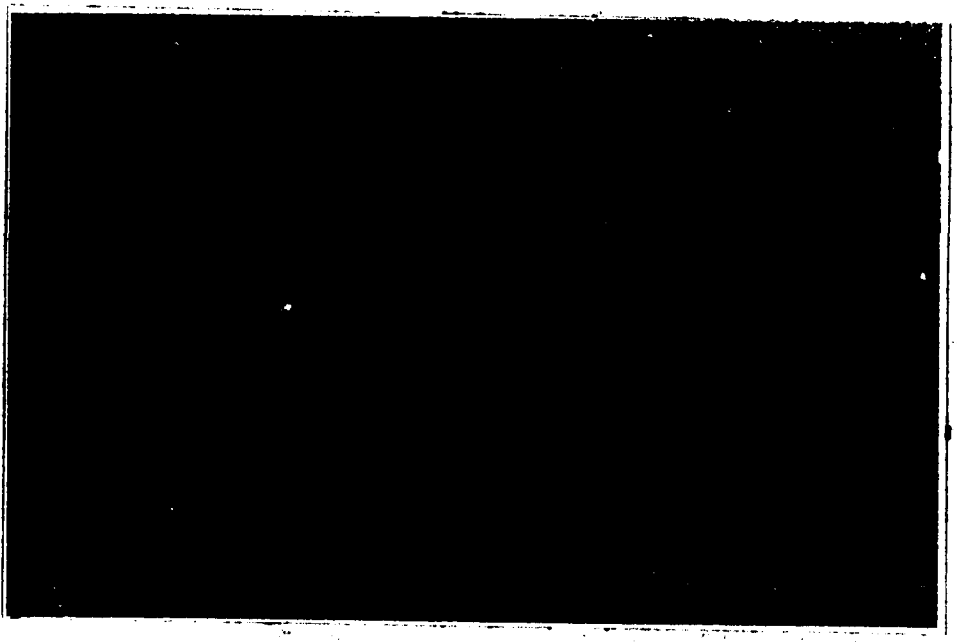


Figure 2. Conductometric titration curves of O.M. preparations.
(a) O.M.I; (b) O.M.II

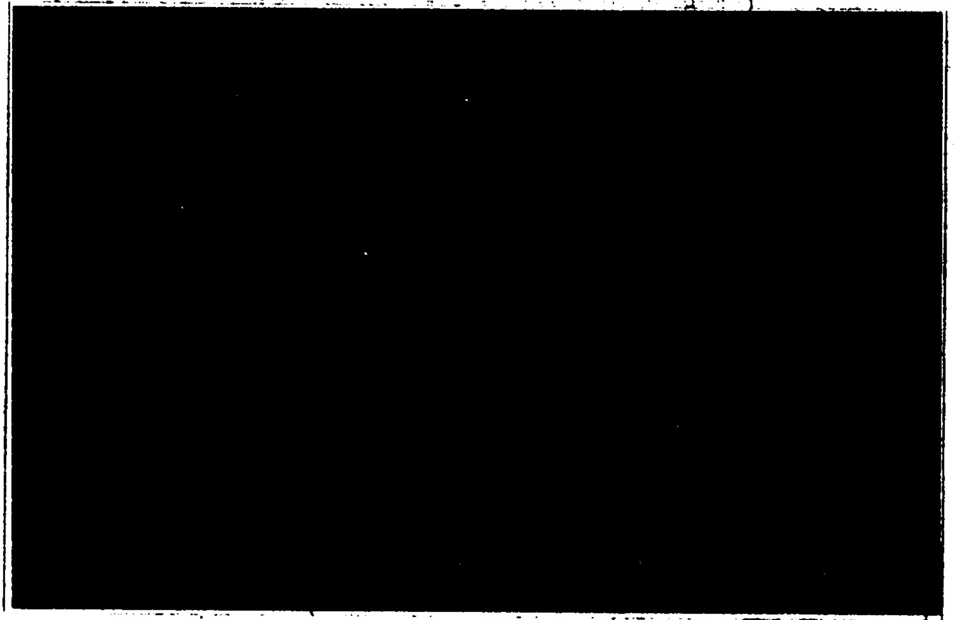
higher pH (6.5-8.0). Whether this was due to some weaker carboxyl groups or phenolic groups capable of chelation, is not clear.

From the values of O.M. and organic carbon, a value of 2.02 was obtained for the conversion of organic carbon to O.M., which is in the range of values reported for the above conversion (Broadbent 1956). No correction was made for ash content.

Electron micrographs of the acid O.M. preparations showed approximately spherical particles of diameter 30-60 Å (Figure 3a). Particles were generally aggregated. When the O.M. was neutralised to pH 7, with NaOH, the spherical shape was almost completely destroyed or only very diffuse (Figure 3b). O.M.II also gave similar pictures. Both O.M. preparations behaved the same way to change in pH. These observations were in agreement with those of Flaig and Beutelspacher (1955) and the electron micrographs of humic acid and sodium humate published by Beutelspacher and Van der Marel (1968). Loss of spherical shape at higher pH values may be due to disaggregation brought about by the breakage of inter and intra molecular hydrogen bonds, increased repulsion between molecules and possibly uncoiling of molecules to attain a stretched

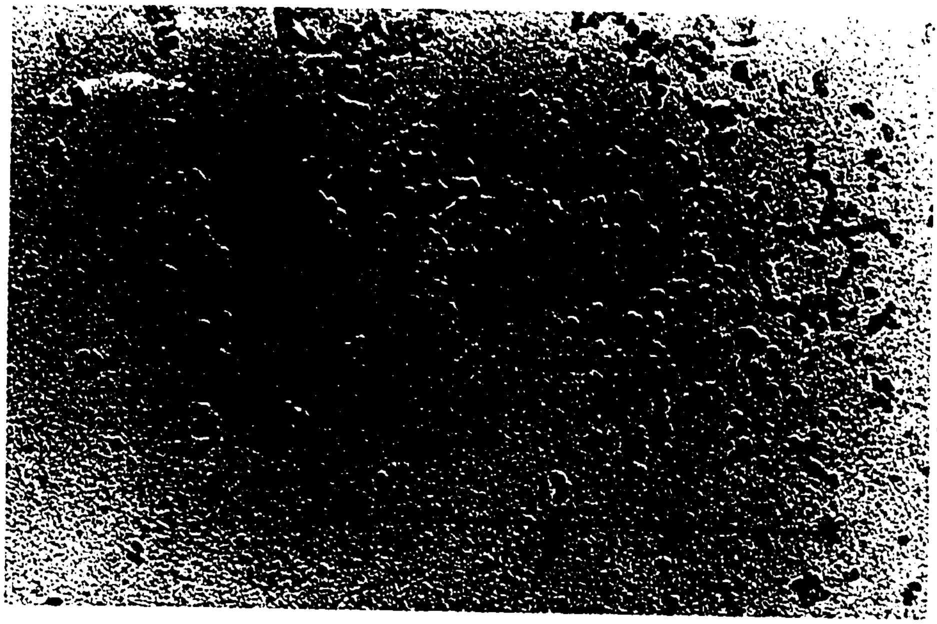


(a) O.M.I at pH 2.86

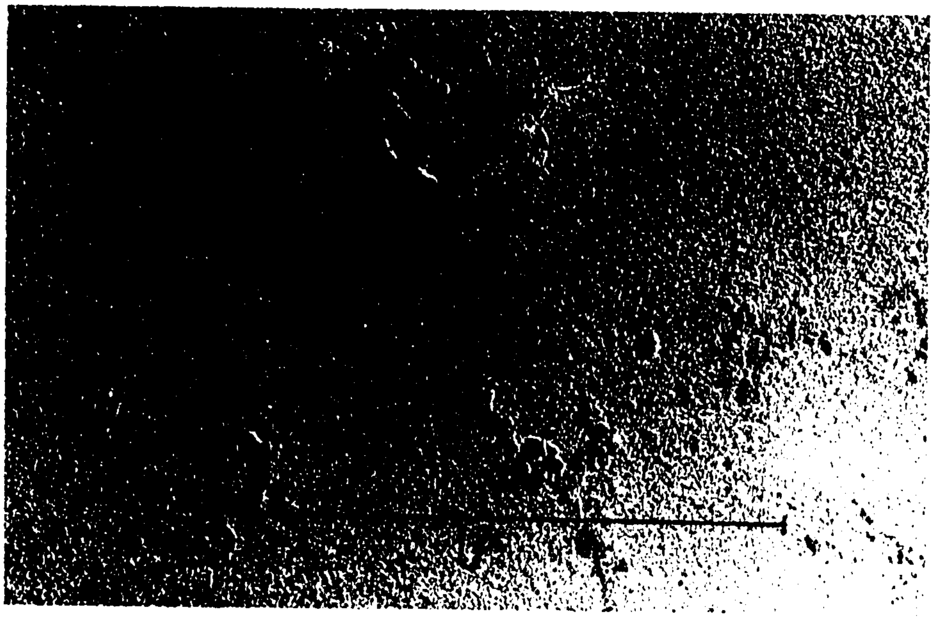


(b) O.M.I at pH 7

Figure 3. Electron micrographs of O.M.I (x70,000)
(a) at pH 2.86 (b) at pH 7



(a) O.M.I at pH 2.86



(b) O.M.I at pH 7

Figure 3. Electron micrographs of O.M.I (x70,000)
(a) at pH 2.86 (b) at pH 7

configuration. These effects were possibly due to increased ionisation of functional groups. O.M. preparations used in this study were X-ray amorphous. No O.M. settled from the suspension when centrifuged at speeds up to 8000 r.p.m. (9000 g).

Infra red spectra (Figure 4) of the O.M. preparations were interpreted according to band assignments given by earlier workers (Wright and Schnitzer 1959; Schnitzer 1965; Felbeck Jr. 1965; Theng et al 1966; Bellamy 1956; Nakamoto 1963). Main absorption bands were as follows: a strong band in the 3400 cm^{-1} region (hydrogen bonded OH), medium bands at 2930 cm^{-1} and at 2850 cm^{-1} (aliphatic C-H stretch), prominent shoulder in the 1720-1690 cm^{-1} region (C=O of COOH and ketonic C=O), strong band in the 1620 cm^{-1} region (aromatic C=C, COO^- and coordinated carboxyls), shoulder in the 1400 cm^{-1} region (COO^-), weak band in the 1230 cm^{-1} region (phenoxy C-O) and a shoulder in the 1025 cm^{-1} region (Si-O of slica due to presence of clay). Spectra of O.M.I and O.M.II were quite similar except that the shoulder in the 1720-1690 cm^{-1} region was less prominent in O.M.II (Figure 4b) than in O.M.I (Figure 4a). The spectra closely resembled those reported for humic acid (Schnitzer 1965) and A_0 horizon O.M. extract (Wright and Schnitzer 1959).

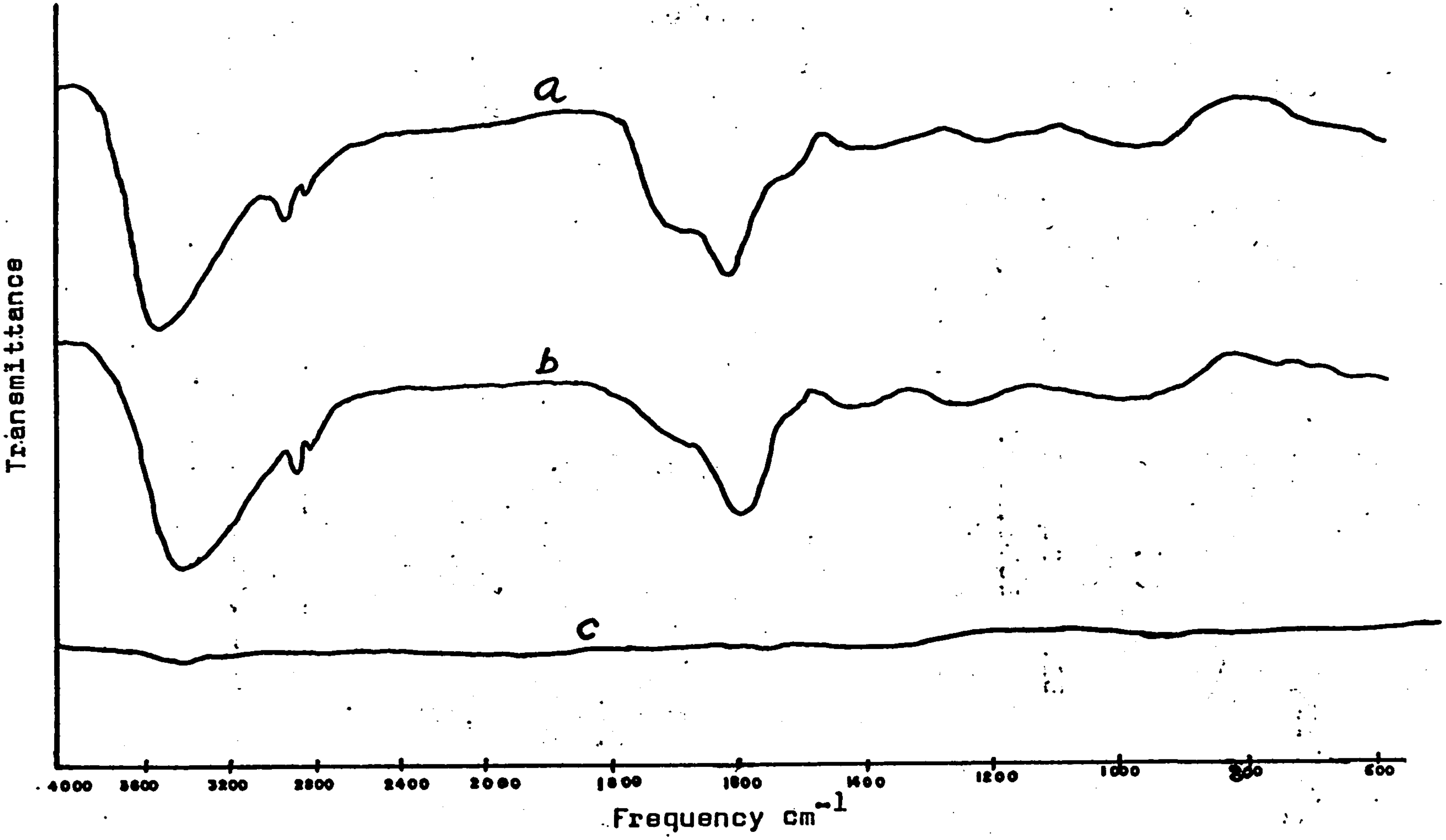


Figure 4. Infra-red spectra of O.M. preparations
(a) O.M.I pH 2.86
(b) O.M.II pH 3.05
(c) KBr
(original recordings are available on file at Soil Science Department, Macdonald College)

Infra red spectra and electron micrographs indicated that the dominant component in the O.M. preparations was "humic acid" which was in agreement with the high percentage of "humic acid" (Table 1) in the preparations.

IV.1.2. Hydroxy Al, Fe polymer solutions

The polymeric hydroxy solutions had respectively pH values of 4.64 and 5.31 for OH:Al molar ratios of 2.5 and 2.7, and 2.90 and 3.12 for OH:Fe molar ratios of 2.5 and 2.7. All solutions were clear to the naked eye when freshly prepared. High OH to metal ion ratios were used to obtain polymers of large size (Rich 1960) to promote formation of coatings on external surfaces of the clay when equilibrated. The $AlCl_3.6H_2O$ used in this study had a free acid (HCl) content of 0.10% (manufacturer's assay). This was inadvertently not taken into consideration when the solutions were prepared. When the required corrections were made, the actual molar ratios were respectively 2.49 and 2.69. However, for simplicity the ratios shall be referred to as 2.5 and 2.7.

IV.1.3. Clays

X-ray diffraction did not show the presence of any mineral other than montmorillonite in the bentonite clay used. The less than 2 µ clay fraction showed a C.E.C. of 85.5 me % at pH 7 and a C.E.C. of 76.6 me % when determined with unbuffered KCl. With buffered KOAc it showed a C.E.C. of 77.1 me % at pH 4.6 and 80.8 me % at pH 5.3. The exchangeable cation on the bentonite clay was dominantly Na with a trace of K. Al saturated clay had a pH of 3.83 and had 71.5 me % of exchangeable Al. Fe saturated clay had a pH of 3.02 and had 124 me % of total Fe (citrate-dithionite extractable) of which only 42.5 me % was exchangeable.

Effective C.E.C. (Coleman _et al_ 1964) of the hydroxy-clays (Table 2) decreased considerably indicating occupation of exchange sites by non-exchangeable polynuclear hydroxy Al species. These results were in agreement with those reported earlier in the literature (Shen and Rich 1962; Barnhisel and Rich 1963; Coleman _et al_ 1964; Turner 1965). In the case of iron hydroxy-clays, the reduction in C.E.C. was very much less. Such a difference in behaviour of Fe hydroxy clays was attributed to the instability of the montmorillonite-iron hydrous oxide complex, the charged polynuclear species undergoing further hydrolysis and precipitated as $Fe(OH)_3$ (Clark and Nichol 1968). However, the inactivation (blocking) of exchange sites on the material was slightly greater than those reported by Clark

TABLE 2. Chemical characteristics of Al and Fe hydroxy-montmorillonites

Al hydroxy clays	$\frac{OH}{Al} = 2.5$	$\frac{OH}{Al} = 2.7$
pH	4.5 (± .05)	5.2 (±.05)
Fixed Al me/100 g	1008	1126
Exchangeable Al me/100 g	7.52	5.12
C.E.C. me/100 g	10.9	7.47
Fe hydroxy clays	$\frac{OH}{Fe} = 2.5$	$\frac{OH}{Fe} = 2.7$
pH	3.3 (±.05)	3.5 (±.05)
Non exchangeable Fe me/100 g	1250	1360
Exchangeable Fe me/100 g	1.42	1.01
C.E.C. me/100 g	38.5	55.1

and Nichol (1968) for clays with OH/Fe molar ratios in the same range. This difference was possibly due to the different methods of preparation of the Fe hydroxy-clay. In the present study, the pH of the Fe hydroxy-clay system was maintained close to that of the original hydroxy polymer solution. The results of blocking of effective charge observed here (Table 2) were in better agreement with those reported by Coleman et al (1964) for bentonite-Fe hydrous oxide systems.

Fixed Al (Table 2) was calculated by subtracting the exchangeable Al and the 26.1 me Al/100 g clay extracted by 0.2 N HCl from Na-montmorillonite (lattice Al), from the total Al extracted by 0.2 N HCl from the Al hydroxy clays. Similarly the exchangeable Fe was deducted from the total Fe obtained in the citrate-dithionite extraction to obtain the amount of non exchangeable Fe. The 2.7 ratio clays contained more Al or Fe than the 2.5 ratio clays (Table 2), possibly due to the smaller positive charge per Al or Fe atom than in the case of 2.5 ratio. The OH to Al 2.5 and 2.7 molar ratio clays increased in weight respectively by 17% and 20% after treatment with polymer solution. Increase in weight of the Fe hydroxy-clays was higher than for Al hydroxy-clays, being respectively 26% and 32% for OH to Fe molar ratios of 2.5 and 2.7.

X-ray diffraction data (Table 3) showed increased basal spacings of the hydroxy-clays which has been attributed to interlayering (Slaughter and Milne 1960; Coleman et al 1964; Shen and Rich 1962; Barnhisel and Rich 1963; Turner and Brydon 1965; Sawhney 1968). Slaughter and Milne (1960) reported that the basal spacing of laboratory prepared Al interlayered montmorillonite was variable and was very sensitive to humidity conditions. The values reported here (Table 3) are very similar to those reported for montmorillonite with OH/Al molar ratios in the same range containing similar amounts of fixed Al (Barnhisel and Rich 1963; Turner and Brydon 1965; Sawhney 1968). Fe hydroxy interlayers were not well defined as those of Al. When the Fe hydroxy clays were heated at 200°C for 24 hrs, no definite X-ray diffraction peaks were obtained. Instead, shoulders extending toward higher spacings were observed (Table 3). It appeared that the Fe interlayers were less organised than the Al interlayers. Similar diffuse X-ray diffraction patterns for hydroxy Fe interlayered montmorillonite were reported in the literature (Rich 1960). No evidence of X-ray crystalline $Al(OH)_3$ or $Fe(OH)_3$ was obtained in the freshly prepared Al or Fe hydroxy clays. Mg or K saturation of the clays prior to heating was not done, as the data were primarily intended

TABLE 3. X-ray diffraction data of Al and Fe hydroxy montmorillonite clays

	Air dry Å	Glycerol solvated Å	6 hrs at 100°C Å	24 hrs at 200°C Å
$\frac{OH}{Al}$ = 2.5-clay	18.8	19.6	16.0	15.4
$\frac{OH}{Al}$ = 2.7-clay	18.5	19.2	16.9	16.6
$\frac{OH}{Fe}$ = 2.5-clay	13.6	17.6	N.D.	11.6*
$\frac{OH}{Fe}$ = 2.7-clay	13.4	17.6	N.D.	11.6*
Na-clay	14.8	18.2	11.9	10.3

*Shoulders extending towards higher spacing

N.D. - not determined

to be used for comparison purposes and not for identification of any particular mineral.

Electron micrographs of the hydroxy clays (Figure 5a,b) showed that the external planar surfaces were coated with hydrous oxide. Both the 2.5 and 2.7 ratio Al or Fe clays gave similar electron micrographs. The surfaces of the hydroxy clays appeared rough in contrast to the smooth surface of the original bentonite (Figure 6). A similar change in surface morphology of hydroxy Al treated vermiculite was reported by De Villiers and Jackson (1967). The density of deposited iron hydrous oxide appeared to be more than that of Al hydrous oxide in the corresponding clay. This is in agreement with the suggestion of Coleman *et al* (1964) that iron hydrous oxide was deposited more on the external surfaces of montmorillonite than Al hydrous oxide. However, it should also be noted that the amount of Fe deposited was more than that of Al (Table 2). Iron hydrous oxide on the clay surface appeared to be more particulate than Al hydrous oxide.

Thus the clay preparations used in this study had hydroxy Al or Fe compounds deposited on both internal and external surfaces. Iron hydroxy clays may have had more hydrous oxide on the external surface than the Al hydroxy

(a) $\frac{OH}{Al}$ = [illegible].5-clay

(b) $\frac{OH}{Al}$ [illegible]-clay

[illegible]

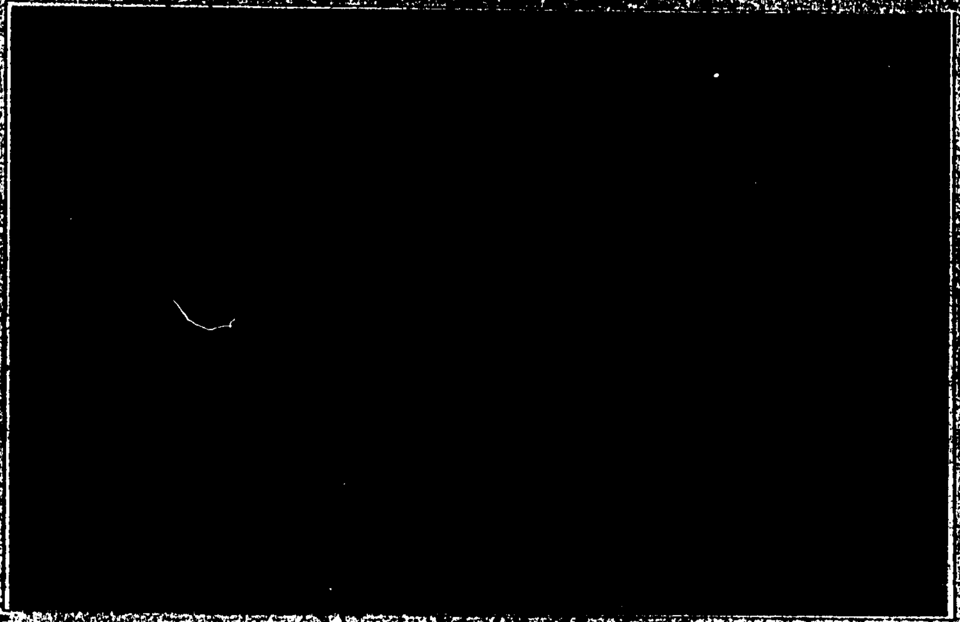


Figure 6. Electron micrograph of sodium bentonite (x70,000)

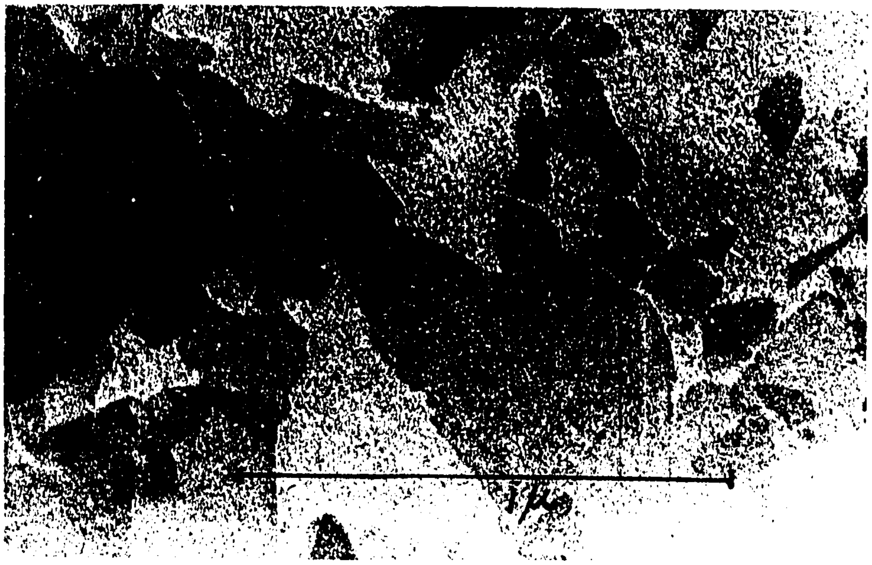


Figure 6. Electron micrograph of sodium bentonite (x70,000)

clays. An appreciable part of the iron hydrous oxide may have been present as $Fe(OH)_3$, especially in the OH/Fe = 2.7 ratio clay as was indicated by the relatively small inactivation of exchange sites.

IV.2. Adsorption studies

IV.2.1. Adsorption isotherms

Adsorption was higher at lower pH values than at pH 7 (Figures 7, 8, 9 and Appendix Tables 1-16). The equilibrium pH at the end of 2 weeks was found to differ from the initial pH by ± 0.15 unit. The Al, Fe hydroxy-clays and the Al^{3+}, Fe^{3+} saturated clays adsorbed much more O.M. than Na saturated clay or H-Na clay at pH 4.5 (pH of OH/Al = 2.5 ratio clay) (Figures 7, 8, 9 and Appendix Tables 1-16). Adsorption isotherms for the Al, Fe hydroxy-clays and Al^{3+}, Fe^{3+} saturated clays were fairly linear at low concentrations of O.M. and curved at higher concentrations showing a tendency to reach adsorption saturation. The linear portion of the isotherms was similar to those reported by Evans and Russell (1959) for H and Ca saturated bentonite. Adsorption values (g O.M./100 g clay) were of the same order of magnitude as reported by Evans and Russell (1959). Per cent adsorption of added O.M. ranged on the average from 90% at low concentrations to 30% at

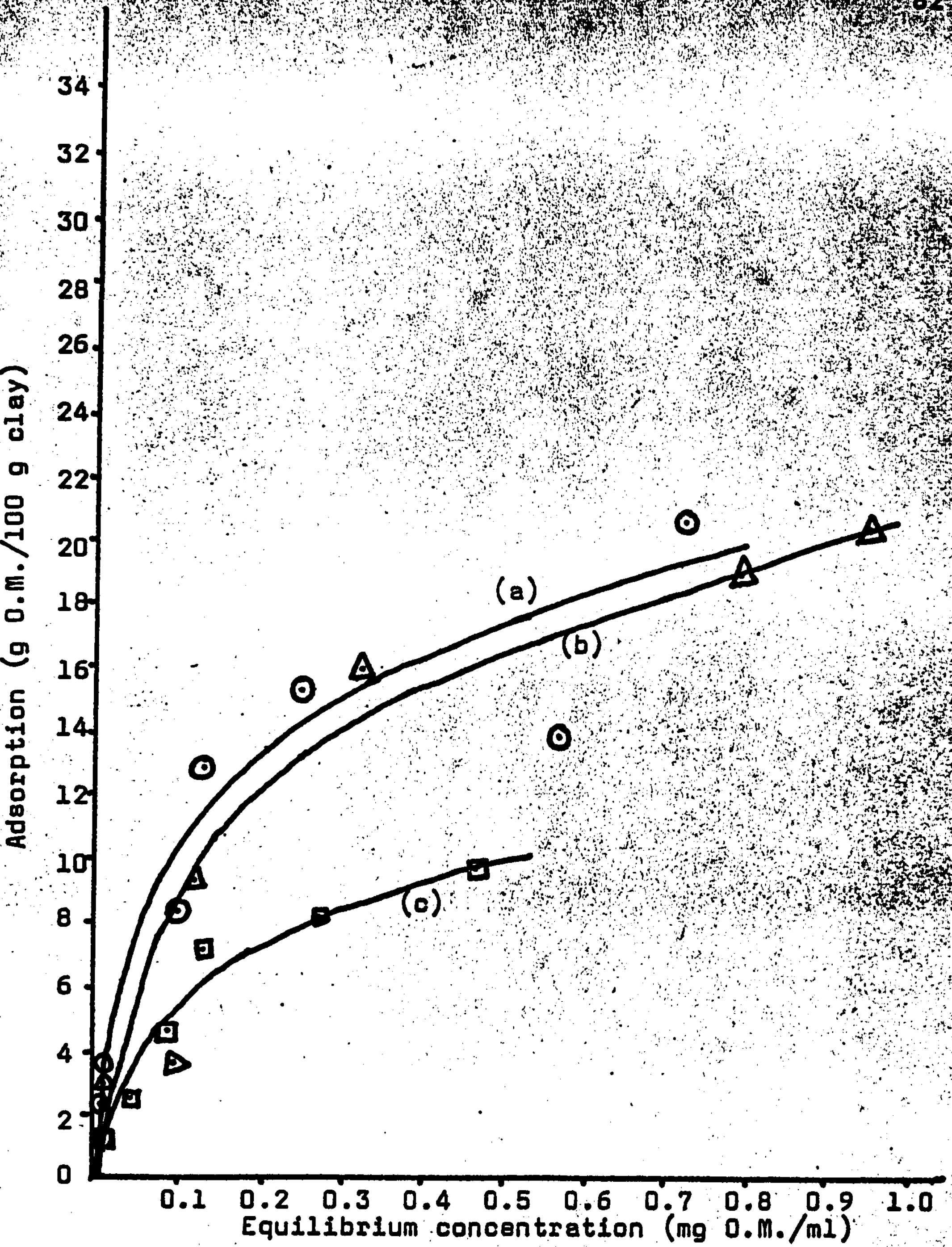


Figure 7. Adsorption isotherms

(a) $\frac{OH}{Al}$ = 2.5 clay-O.M.I (pH 4.5) (⊙)

(b) $\frac{OH}{Al}$ = 2.5 clay-O.M.II (pH 4.5) (△)

(c) $\frac{OH}{Al}$ = 2.5 clay-O.M.I (pH 7.0) (⊡)

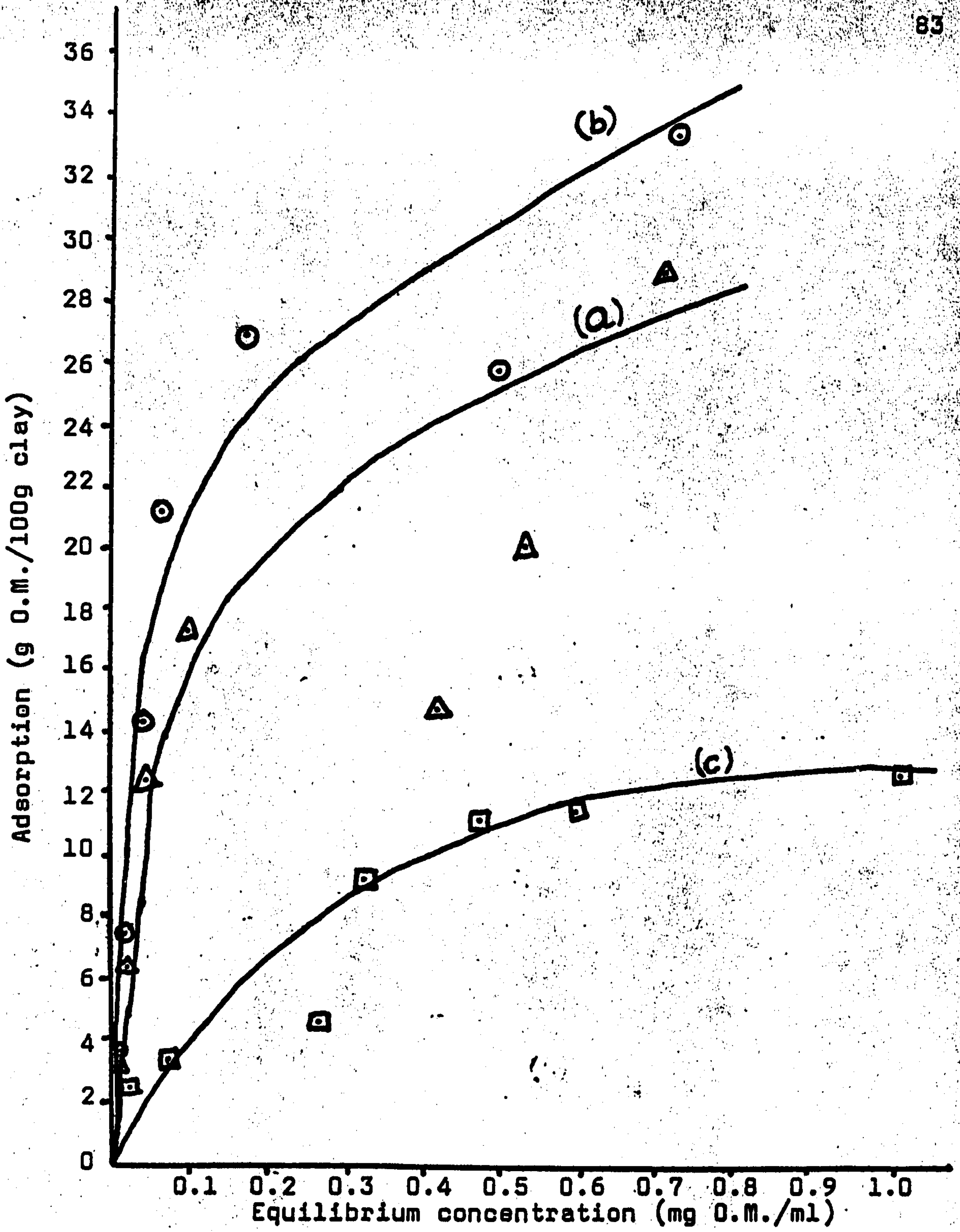


Figure 8. Adsorption isotherms

(a) $\frac{\text{OH}}{\text{Fe}}$ = 2.5-clay-O.M.I (pH 3.3) (⊙)

(b) $\frac{\text{OH}}{\text{Fe}}$ = 2.5-clay-O.M.II (pH 3.3) (△)

(c) $\frac{\text{OH}}{}$ = 2.5-clay-O.M.I (pH 7.0) (⊡)

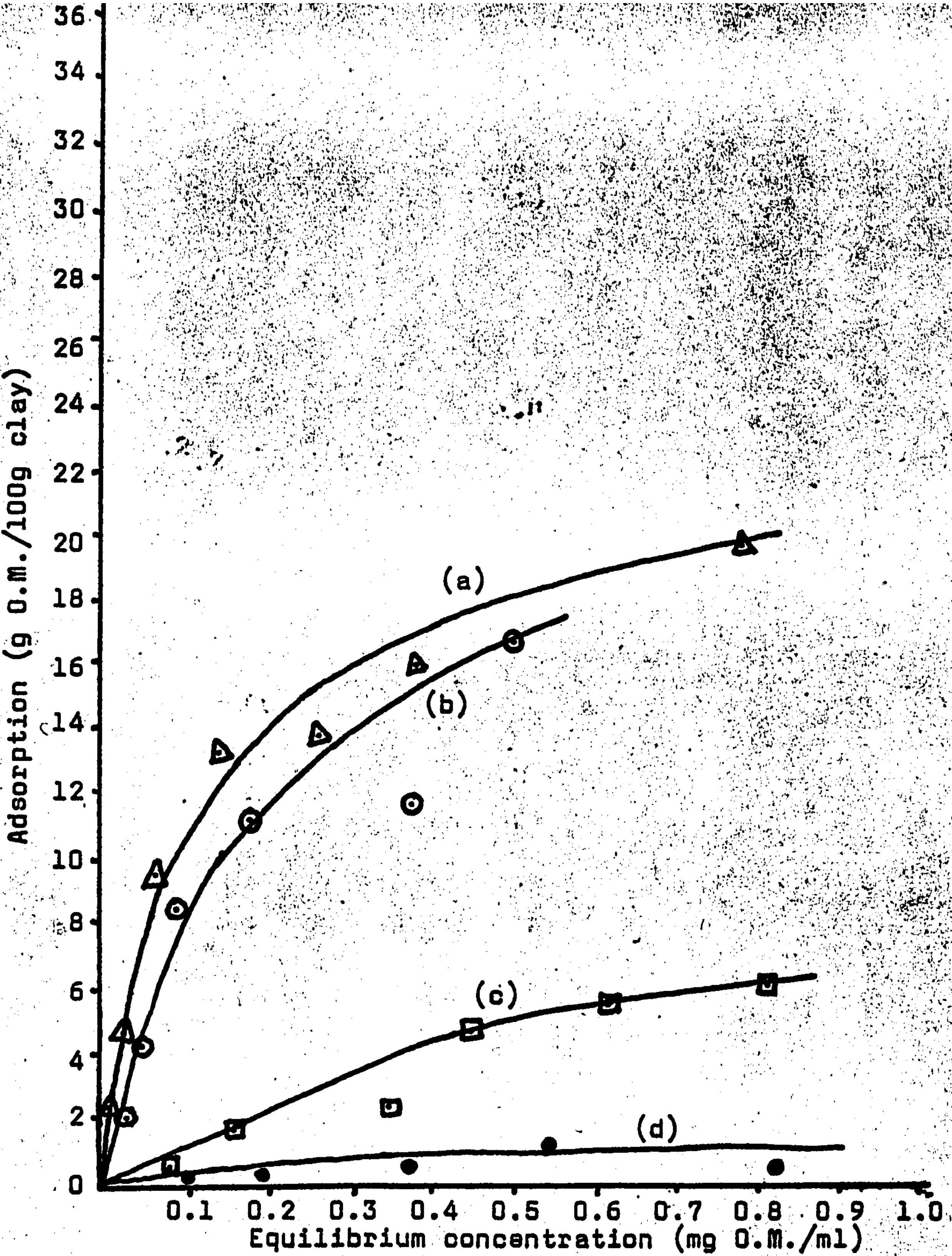


Figure 9. Adsorption isotherms

(a) Fe^{3+}-clay-O.M.I (pH 3.0) (△)
(b) Al^{3+}-clay-O.M.I (pH 3.8) (⊙)
(c) H^{+}-Na^{+}-clay-O.M.I (pH 4.5) (⊡)
(d) Na^{+}-clay-O.M.I (pH 7.0) (●)

higher concentrations. Per cent adsorption was higher at low pH values.

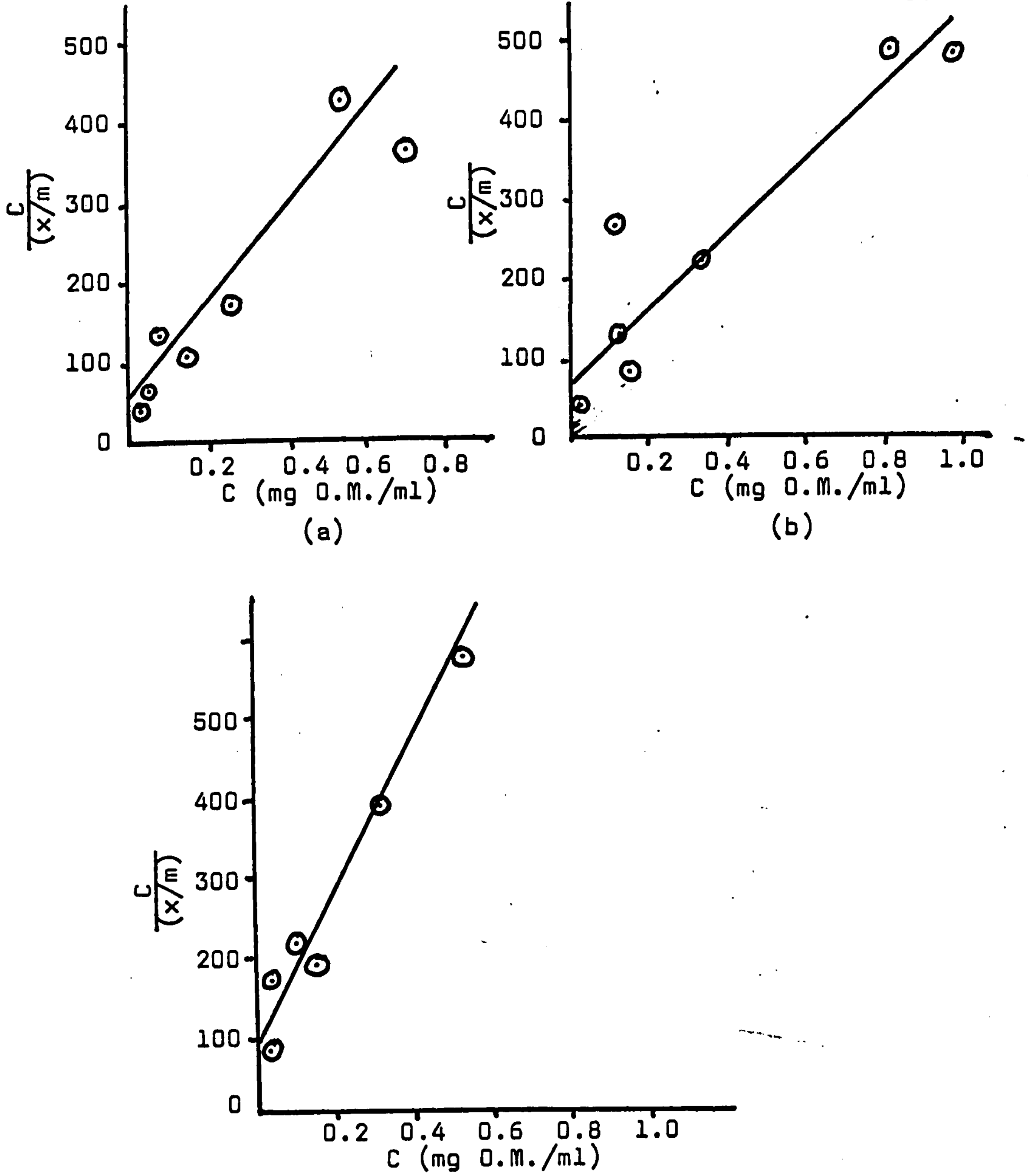
Conformity to Langmuir adsorption isotherm was tested by using the equation $\frac{C}{(x/m)} = \frac{1}{Kb} + \frac{C}{b}$ (Olsen and Watanabe 1957; Hemwall 1963) where C is the equilibrium concentration of O.M., x/m the amount of O.M. adsorbed per unit weight of clay, b the adsorption maximum and K a constant related to the bonding energy of the adsorbent for the adsorbate.

Simple correlation coefficients of $\frac{C}{(x/m)}$ with C (Table 4) and the corresponding regression equations were calculated. Values of b and K (Table 4) were calculated from the slope and intercept. Only approximate conformity to Langmuir isotherm (Figures 10, 11 and 12) was observed, the data deviating from it at both low and high concentrations of O.M. Even though the correlation coefficients (Table 4) were high, the standard error of the estimates was also high and the experimental points were dispersed around the regression lines (Figures 10, 11, 12). The Langmuir adsorption isotherm has been applied to single adsorbate-multicomponent adsorbent systems (Olsen and Watanabe 1957; Shapiro and Fried 1959) and to multicomponent adsorbate-single adsorbent system (Saini and MacLean 1966).

TABLE 4. Summary of simple correlation coefficients ($\frac{C}{(x/m)}$ with C) and Langmuir constants b and K for the adsorption of O.M. on clay preparations

System	pH	Correlation coefficient	b g O.M./ 100g clay	K
$\frac{OH}{Al}$ = 2.5-clay-O.M.I	4.5	0.95**	20.0	9.7
$\frac{OH}{Al}$ = 2.5-clay-O.M.II	4.5	0.92**	25.0	4.4
$\frac{OH}{Al}$ = 2.5-clay-O.M.I	7.0	0.98**	11.1	9.6
$\frac{OH}{Al}$ = 2.7-clay-O.M.I	5.2	0.95**	20.4	11.0
$\frac{OH}{Al}$ = 2.7-clay-O.M.II	5.2	0.95**	26.8	9.7
$\frac{OH}{Al}$ = 2.7-clay-O.M.I	7.0	0.95**	12.9	9.6
$\frac{OH}{Fe}$ = 2.5-clay-O.M.I	3.3	0.91**	24.4	12.5
$\frac{OH}{Fe}$ = 2.5-clay-O.M.II	3.3	0.98**	34.5	12.8
$\frac{OH}{Fe}$ = 2.5-clay-O.M.I	7.0	0.92**	13.4	4.0
$\frac{OH}{Fe}$ = 2.7-clay-O.M.I	3.5	0.97**	30.3	14.0
$\frac{OH}{Fe}$ = 2.7-clay-O.M.II	3.5	0.98**	35.7	11.7
$\frac{OH}{Fe}$ = 2.7-clay-O.M.I	7.0	0.94**	14.9	14.9
Al^{3+}-clay-O.M.I	3.8	0.95**	17.8	7.2
Fe^{3+}-clay-O.M.I	3.0	0.98**	19.6	9.0
H^{+}-Na^{+}-clay-O.M.I	4.5	0.63	11.5	0.9
Na^{+}-clay-O.M.I	7.0	0.96**	1.1	0.3

**significant at 1% level of significance



(a)

(b)

(c)

Figure 10. Langmuir adsorption isotherms

(a) $\frac{OH}{Al}$ = 2.5-clay-O.M.I (pH 4.5)

(b) $\frac{OH}{Al}$ = 2.5-clay-O.M.II (pH 4.5)

(c) $\frac{OH}{Al}$ = 2.5-clay-O.M.I (pH 7.0)

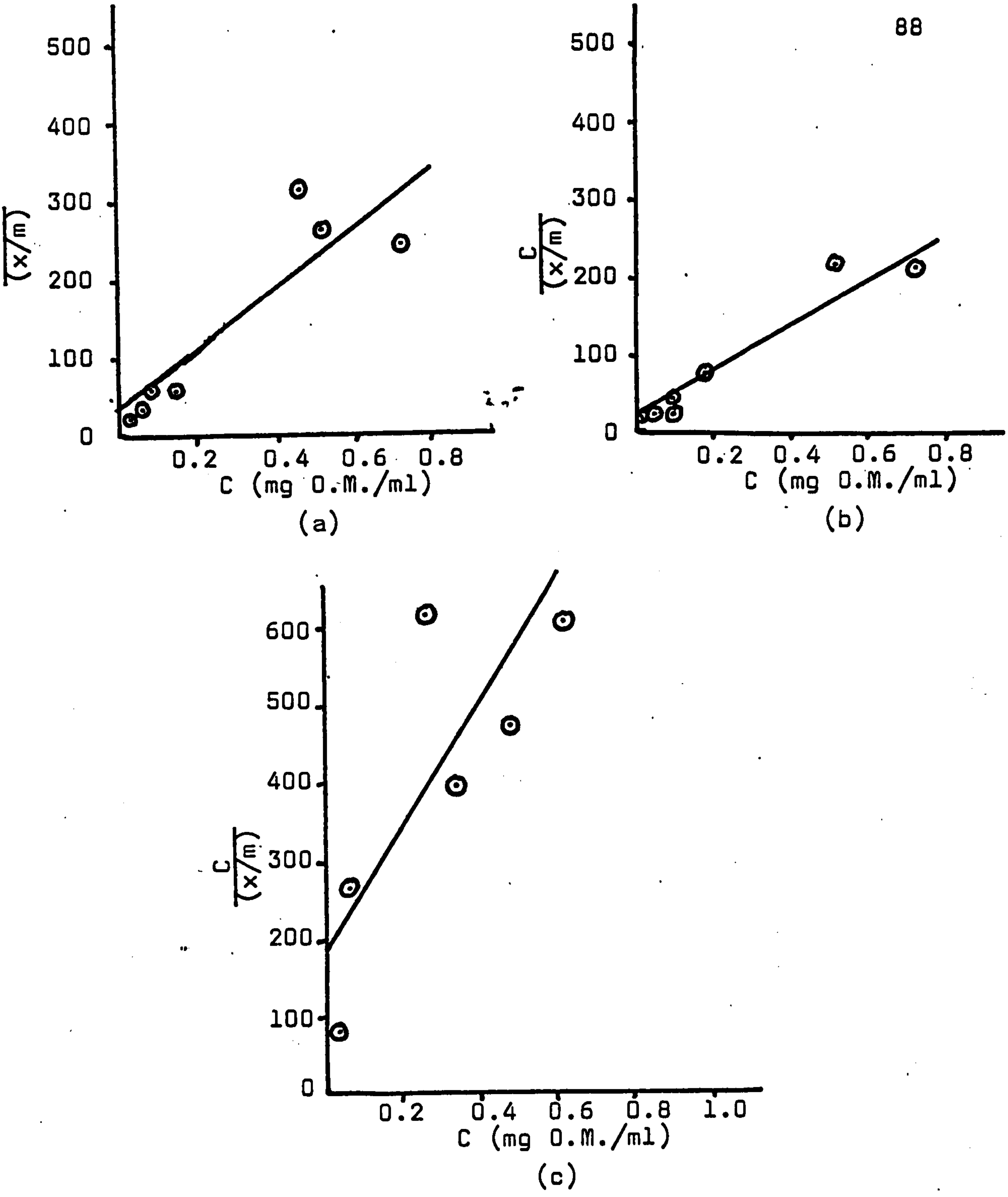


Figure 11. Langmuir adsorption isotherms

(a) $\frac{OH}{Fe}$ = 2.5-clay-O.M.I (pH 3.3)
(b) $\frac{OH}{Fe}$ = 2.5-clay-O.M.II (pH 3.3)
(c) $\frac{OH}{Fe}$ = 2.5-clay-O.M.I (pH 7.0)

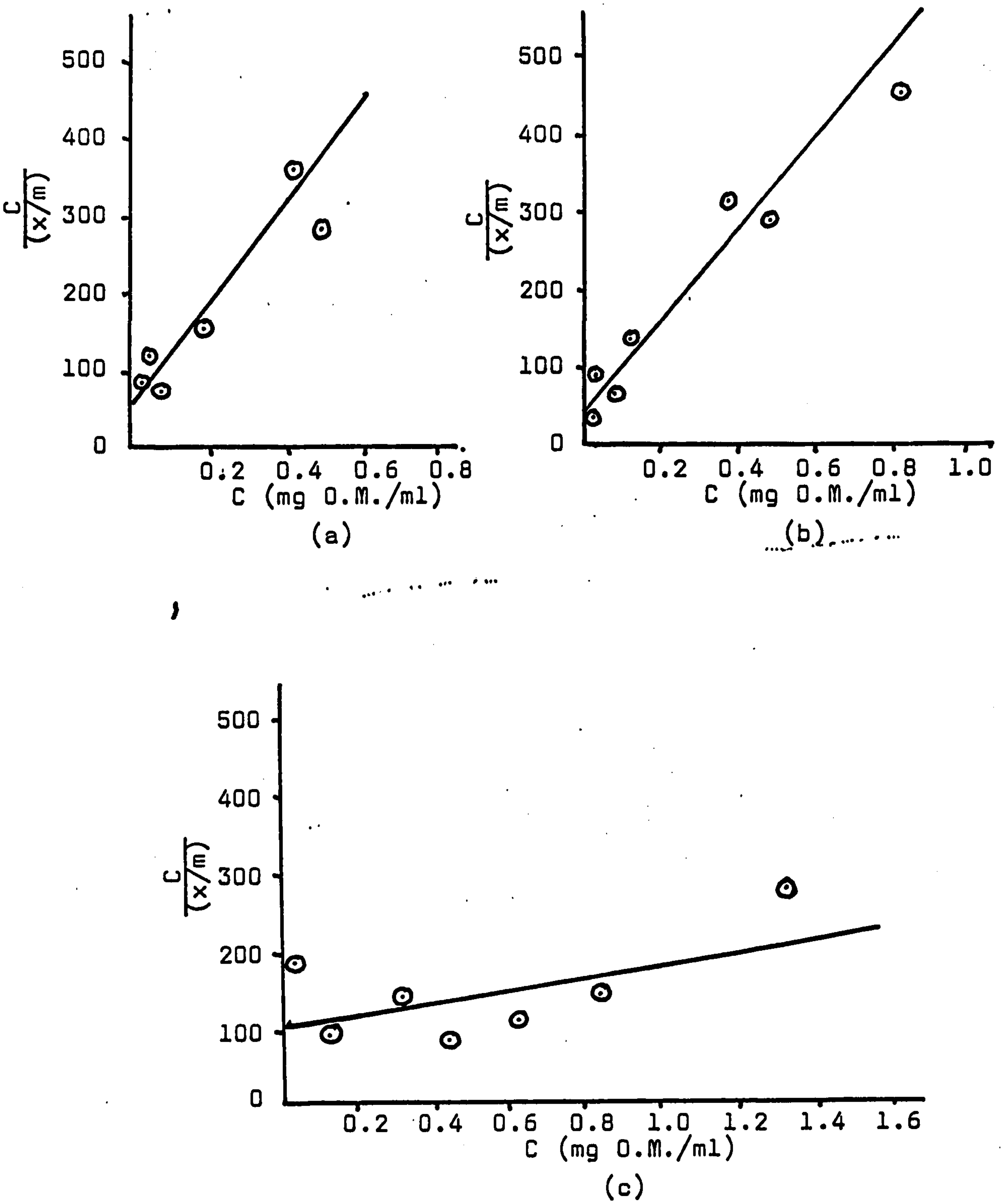


Figure 12. Langmuir adsorption isotherms
(a) Al^{3+}-clay-O.M.I (pH 3.8)
(b) Fe^{3+}-clay-O.M.I (pH 3.0)
(c) H-Na-clay-O.M.I (pH 4.5)

In the systems studied here, the adsorbate was a multi-component heterogeneous system whose components were less defined than those used by Saini and MacLean (1966). Hence the application of Langmuir isotherm may be questionable despite approximate conformity. It is rather difficult to give a precise interpretation to the values of b and K. Values of K may be regarded as a sort of a quantity related to the average bonding energy.

The values of adsorption maximum (Table 4) were not unreasonable. Evans and Russell (1959) reported a value of 18.4g organic carbon per 100g clay (approximately 30g O.M./100g clay) for Ca bentonite and still the adsorption maximum was not reached. In the case of H-Na clay, saturation was reached at about 5-6g O.M./100g clay (experimental value, Figure 9c and Appendix Table 15), whereas the Langmuir isotherm predicted an adsorption maximum of 11.1g O.M./100g clay. K values for the hydroxy clays (at low pH values) were generally higher than those for Al^{3+} and Fe^{3+} saturated clays (Table 4). This indicated that the O.M. was held stronger by the hydroxy clays than by the Al or Fe saturated clays. A stronger bonding to the hydroxy-clays may be due to the higher charge on the polynuclear Al, Fe hydroxy ions and to the possibility of hydrogen bonding of carboxyl groups in O.M. to hydroxyls in hydrous oxides. Hydrogen bonding is not possible with Al^{3+} or Fe^{3+} ions on clay surface. At pH 7, the K values for Fe hydroxy-clays decreased, but the values were not consistent (Table 4) to make any definite conclusion.

There was not much difference in adsorption between the 2.5 and 2.7 ratio clays in either case. Two opposing factors may have caused this. The higher pH value of the 2.7 ratio clays would have decreased adsorption due to (i) decreased positive charges on clay edges, (ii) increased competition between OH and carboxyls for coordination positions around Al or Fe. On the other hand, the higher amount of hydrous oxide (Table 2), in the 2.7 ratio clays, possibly on the external surface, would have increased adsorption. Fe hydroxy-clays adsorbed more than the Al-hydroxy-clays. This may have been due to the fact that Fe hydrous oxide was possibly deposited mainly on the external surface of the clay, whereas a large portion of Al-hydrous oxide went into the interlayer positions (section IV.1.3). The lower pH of the Fe hydroxy-clays may also have been responsible for higher adsorption (due to higher clay-edge positive charges at lower pH values). Fe hydrous oxide may also have been present partly as $Fe(OH)_3$ as a separate phase in the Fe hydroxy-clays. At pH 7, the difference between Al and Fe hydroxy-clays in the maximum amount adsorbed was smaller. O.M.II was generally adsorbed in greater amounts than O.M.I, possibly due to its higher equivalent weight.

Conformity to Langmuir isotherm has generally been interpreted as indicating monolayer adsorption (Mortensen 1962). However, Saini and MacLean (1966) pointed out that approximate conformity to Langmuir isotherm does not necessarily mean monolayer adsorption. Simha _et_ _al_ (1953) showed that adsorption of a polymer occurred through extended segments of the polymer being anchored to the adsorbent. Such a phenomenon could account for the high adsorption values obtained.

IV.2.2. Desorption of adsorbed O.M.

Acid O.M. was adsorbed to a greater extent than neutralised O.M. (pH 7) (Tables 5 and 6). In the desorption experiment, the clay preparations were not saturated with O.M. to the full capacity before desorption. Water (distilled) desorbed only small amounts, generally less than 5% of total adsorbed, except in the case of Na-clay where 15-16% was desorbed. Desorption by 0.5 N Na_2CO_3 (pH 10.5) ranged from 67-84% (Tables 5 and 6) for the various hydroxy-clays and almost completely in the case

TABLE 5. Desorption of O.M. adsorbed by Al hydroxy-clays

	Equilibrium pH	Total adsorbed	Desorbed by H_2O	Desorbed by 0.5 N Na_2CO_3	Desorbed by 0.5 N NaOH
		g O.M./100g clay			
Acid O.M.I (pH 2.86)					
$\frac{OH}{Al}$ = 2.5-clay	4.01	8.71	0.09(1)*	6.45(74)	2.02(23)
$\frac{OH}{Al}$ = 2.7-clay	4.40	9.20	0.07(1)	6.82(74)	2.40(26)
Al^{3+}-clay	3.28	6.04	0.12(2)	5.12(85)	0.95(16)
Na^{+}-clay	4.86	0.97	0.15(16)	0.83(86)	-
Acid O.M.II (pH 3.05)					
$\frac{OH}{Al}$ = 2.5-clay	4.05	9.47	0.07(1)	7.19(76)	1.74(18)
$\frac{OH}{Al}$ = 2.7-clay	4.48	9.44	0.04(0.5)	7.00(74)	2.16(23)
Al^{3+}-clay	3.34	6.08	0.42(7)	5.04(82)	1.08(18)
Na^{+}-clay	4.95	1.74	0.28(16)	1.42(82)	-
Neutralised (pH 7) O.M.I					
$\frac{OH}{Al}$ = 2.5-clay	6.75	3.52	0.11(3)	2.89(82)	0.63(18)
$\frac{OH}{Al}$ = 2.7-clay	6.90	4.08	0.08(2)	3.22(79)	1.01(25)
Neutralised (pH 7) O.M.II					
$\frac{OH}{Al}$ = 2.5-clay	6.78	4.48	0.10(2)	3.76(84)	0.84(19)
$\frac{OH}{Al}$ = 2.7-clay	6.92	4.36	0.08(2)	3.55(81)	0.59(14)

Standard error 0.12

*Figures in parentheses are amounts desorbed expressed as per cent of total O.M. adsorbed.

TABLE 6. Desorption of O.M. adsorbed on Fe hydroxy-clays

	Equilibrium pH	Total adsorbed	Desorbed by H_2O	Desorbed by 0.5 N Na_2CO_3	Desorbed by 0.5 N NaOH
		←	g O.M./100g clay		→
<u>Acid O.M.I (pH 2.86)</u>					
$\frac{OH}{Fe}$ = 2.5-clay	3.01	9.74	0.07(1)*	6.49(67)	2.83(29)
$\frac{OH}{Fe}$ = 2.7-clay	3.20	9.83	0.16(2)	6.68(68)	3.07(31)
Fe^{3+}-clay	2.95	7.01	0.07(1)	5.42(77)	1.46(21)
<u>Acid O.M.II (pH 3.05)</u>					
$\frac{OH}{Fe}$ = 2.5-clay	3.05	10.32	0.11(1)	6.80(66)	2.59(25)
$\frac{OH}{Fe}$ = 2.7-clay	3.27	10.43	0.13(1)	7.27(70)	2.68(26)
Fe^{3+}-clay	2.95	7.01	0.14(2)	5.42(77)	1.38(20)
<u>Neutralised (pH 7) O.M.I</u>					
$\frac{OH}{Fe}$ = 2.5-clay	5.96	4.74	0.10(2)	3.50(74)	1.06(22)
$\frac{OH}{Fe}$ = 2.7-clay	6.03	4.86	0.07(1)	3.34(69)	1.06(22)
<u>Neutralised (pH 7) O.M.II</u>					
$\frac{OH}{Fe}$ = 2.5-clay	6.08	5.27	0.09(2)	3.70(70)	0.98(19)
$\frac{OH}{Fe}$ = 2.7-clay	6.12	5.43	0.25(5)	3.81(70)	1.07(20)

Standard error 0.09

*Figures in parentheses are amounts desorbed expressed as per cent of total O.M. adsorbed of Na-clay. The hydroxy-clays retained more O.M. undesorbed by Na_2CO_3 than Al or Fe saturated clays. Less O.M. was desorbed by Na_2CO_3 in the Fe systems than in the Al systems. NaOH (0.5 N) desorbed the remaining O.M. in all cases (15-32%). Sen (1960) reported higher percentages (20-80%) for adsorbed O.M. not desorbed by 0.5 N Na_2CO_3 in the case of Al and Fe saturated clays. It has also been reported that iron was more difficult to extract from iron-O.M. complexes than aluminum from aluminum-O.M. complexes (Schnitzer and Skinner 1964; Russell 1963). Schwertmann (1966); Schwertmann et al (1968) reported that O.M. was retained by ferric hydroxide even under very alkaline conditions. The results reported here are in general agreement with these earlier reports. Results of the desorption experiment (Tables 5 and 6) showed that the mechanisms of O.M. retention were pH dependent and that there was a competition between OH ions and O.M. for sites of adsorption.

Three possible mechanisms operating either singly or in combination could explain the above observations. The mechanisms are: (a) electrostatic bridging of O.M. by the positive charged hydroxy Al or Fe polymeric ions or direct attachment of O.M. to positive edge sites on the clay; (b) hydrogen bonding of (i) the carboxyl or carboxylate group of

O.M. to the OH of the hydroxy Al, Fe polymeric ions (or hydrous oxides) on clay surfaces or to the OH of clay edges, (ii) the carboxylic acid group of O.M. to oxygen on clay surface (through the OH of COOH); (c) coordination of carboxyls of O.M. to Al or Fe atoms of the hydrous oxides either by replacement of OH groups or by occupation of vacant coordination positions (possibly occupied by water).

If electrostatic bridging was operative, then as the pH was raised, the positive charge on the hydrous oxides would have decreased releasing O.M. held by such linkages. Positive charges on clay edges also would have decreased or disappeared at higher pH values and the O.M. held by such positive spots would also have been released. The amount of positive charges on clay edges was small, being 8.4 me and 4.7 me positive charge per 100g clay, respectively at pH 4.6 and pH 5.3. These values were obtained from the difference in C.E.C. values at pH 7 and at pH 4.6 and 5.3, of the original bentonite clay (section IV.1.3). Assumption was made that the amount of edge positive charge at pH 7 is zero. Assuming only simple electrostatic bonding between O.M. and clay edges, the edge positive charges would account only for a maximum adsorption of 3.5g O.M. at pH 4.6 and 2g O.M. at pH 5.3 per 100g clay (basis of charge equivalence). However, the simple electrostatic mechanism (including bridging) does not explain that part of O.M. retained, undesorbed by 0.5 N Na_2CO_3 at pH 10.5, as it is unlikely that there would be any residual positive charge at this pH.

O.M. hydrogen bonded to the clay surface through OH of COOH (Type I, section II.1.2.3.2) of the O.M. would have been readily desorbed as the pH was raised. However, O.M. hydrogen bonded through oxygen of the carboxyl group or carboxylate ion (Types II and III, section II.1.2.3.2) may not have been readily desorbed by Na_2CO_3. Presence of a large number of OH groups on the hydroxy Al, Fe compounds plastered onto the clay surface would have enhanced the formation of hydrogen bonds of the latter types. Hydrogen bonding of the OH attached to Al and Fe has been shown to occur in diaspore and lepidocrocite (Pauling 1960). O.M. bonded to Al hydrous oxides would have been desorbed by NaOH when the Al hydrous oxides were dissolved.

If the coordination mechanism (c) was operative, the O.M. could have been adsorbed at lower pH values by the replacement of OH bound to Al or Fe hydrous oxide by carboxyl group or by the carboxylate group, occupying vacant coordination positions (possibly occupied by H_2O). O.M.

adsorbed in this manner would have been desorbed progressively by a reversal of the reaction, as the pH was raised. The amount of O.M. undesorbed by Na_2CO_3 may possibly be due to formation of strong chelates, where multiple bonds are involved. A still higher pH or higher concentration of OH ions would be required to displace such carboxyls. It is of interest at this point, to refer to a report that humic acid chelates of Al and Fe were only partly hydrolysed in slightly alkaline medium to hydroxochelates and were completely hydrolysed only in strongly alkaline medium (Kawaguchi and Kyuma 1961). The exact pH values were not reported.

Presence of higher charged polynuclear Al or Fe ions on clay surfaces would have reduced or practically eliminated the diffuse ion layer around the clay particles. This would have facilitated closer approach of the O.M. to the clay surface by reducing the zeta potential (Ahlrichs 1962; Mortensen 1962). Such a situation would have enhanced the formation of multiple hydrogen bonds between O.M. and hydrous oxides on clay surface and also would have brought about the operation of London-Van der Waals forces, which would have further strengthened the bonding. In the case of Na-clay no such strong bonding was possible and the small amount of O.M. adsorbed was completely desorbed by Na_2CO_3.

Thus the explanation for the retention of O.M. undesorbed by 0.5 N Na_2CO_3 is the possible formation of coordination bonds (possibly chelate type) between O.M. and hydrous oxides on clay surface and augmentation of this by multiple hydrogen bonds and Van der Waals forces. The hydroxy clays retained higher percentage of O.M. undesorbed by Na_2CO_3 than the Al or Fe saturated clays. Although the same type of coordination or complex formation should be possible in either case, chances of formation of pH stable hydrogen bonds of the types II and III (section II.1.2.3.2) were much more in the case of hydroxy clays than in the case of Al^{3+} or Fe^{3+} saturated clays. Further, the amount of Al or Fe (total) was higher in the hydroxy clays than in the Al^{3+} or Fe^{3+} saturated clays. These may be the reasons for the higher percentage retention of O.M. by the hydroxy clays. Further evidence on the existence of a coordination mechanism (anion penetration type) shall be presented later.

IV.2.3. Adsorption sites

X-ray diffraction data (Table 7) did not show any increase in basal spacing of the hydroxy-clays after reaction with O.M.I. The d spacings after heat treatments etc. were almost the same as those of the corresponding hydroxy-clays (Table 3). It is unlikely that any O.M. was

TABLE 7. X-ray diffraction data of hydroxy-clay-O.M. complexes

	Air dry Å	Glycerol solvated Å	6 hrs at 100^oC Å	24 hrs at 200^oC Å
$\frac{OH}{Al}$ = 2.5-clay-O.M.I(pH 2.86)	18.1	19.2	15.7	14.9
$\frac{OH}{Al}$ = 2.5-clay-O.M.I(pH 7.0)	18.2	18.8	15.7	15.7
$\frac{OH}{Al}$ = 2.7-clay-O.M.I(pH 2.86)	18.1	19.2	16.9	16.6
$\frac{OH}{Al}$ = 2.7-clay-O.M.I(pH 7.0)	18.1	18.8	16.6	16.6
$\frac{OH}{Fe}$ = 2.5-clay-O.M.I(pH 2.86)	12.5	18.4	N.D.	12.2*
$\frac{OH}{Fe}$ = 2.5-clay-O.M.I(pH 7.0)	12.6	18.4	N.D.	10.5*
$\frac{OH}{Fe}$ = 2.7-clay-O.M.I(pH 2.86)	12.4	17.6	N.D.	11.9*
$\frac{OH}{Fe}$ = 2.7-clay-O.M.I(pH 7.0)	12.1	18.4	N.D.	10.2*

*Shoulders extending towards higher spacing

N.D. - Not determined

lost at 100 or 200°C. This showed that the O.M.I preparation was not adsorbed in the interlamellar space.

Electron micrographs of the O.M.I-hydroxy-clay complexes (Figures 13, 14, 15) showed both edge face and planar face association of O.M. The electron micrographs of the Fe hydroxy-clay-O.M.I complexes were complicated due to the presence of particulate Fe hydroxide (Figure 15a). However, on closer look, the spherical O.M. particles (shown by arrow) could be distinguished from the irregular iron hydroxide particles. Equilibrium pH values were the same as those reported in Tables 5 and 6. At high pH values (Figures 13c, 14b, c), the spherical shape of the O.M. was diffuse or completely lost. Similar observation was made with the O.M. alone (Figures 3a, b, section IV.1.1). Figure 16 shows the Na clay-O.M.I complex where only a very small amount was adsorbed (possibly on the clay edges). A point of interest is the appearance of pseudo-hexagonal crystals, possibly gibbsite (Gastucha and Mortland 1964) on the control Al hydroxy-clays (nearly 4 weeks after preparation of the hydroxy-clays), but not on the O.M. treated ones. The effect of O.M. on the formation of crystalline $Al(OH)_3$ shall be discussed in a later section.

(a) $\frac{OH}{Al}$ = 2.5-clay

(b) $\frac{OH}{Al}$ = 2.5-clay-O.M.I(pH 2.86)

Figure 13. Electron micrographs of clay-O.M. complexes (x70,000)
(a) $\frac{OH}{Al}$ = 2.5-clay (4 weeks after preparation)
(b) $\frac{OH}{Al}$ = 2.5-clay-O.M.I(pH 2.86)

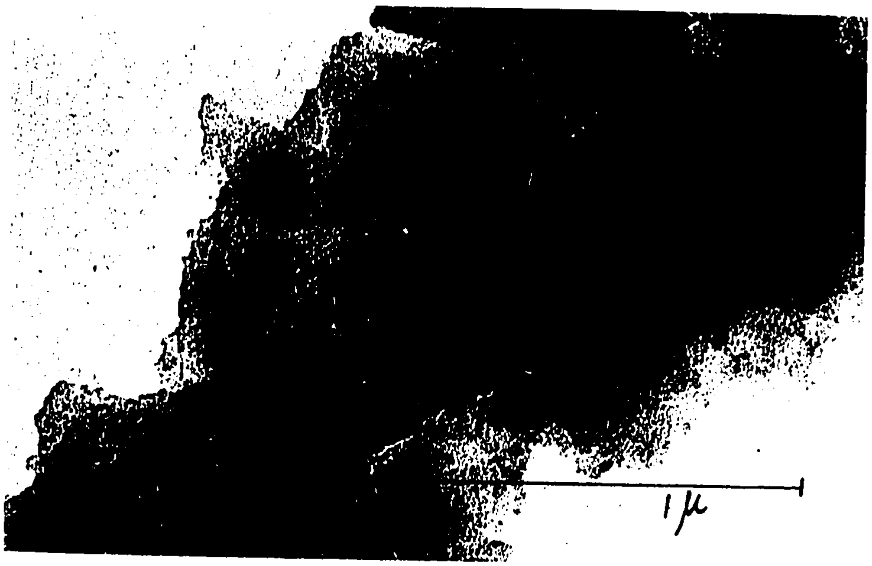
(a) $\frac{OH}{Al}$ = 2.5-clay

(b) $\frac{OH}{Al}$ = 2.5-clay-O.M.I(pH 2.86)

Figure 13. Electron micrographs of clay-O.M. complexes (x70,000)

(a) $\frac{OH}{Al}$ = 2.5-clay (4 weeks after preparation)

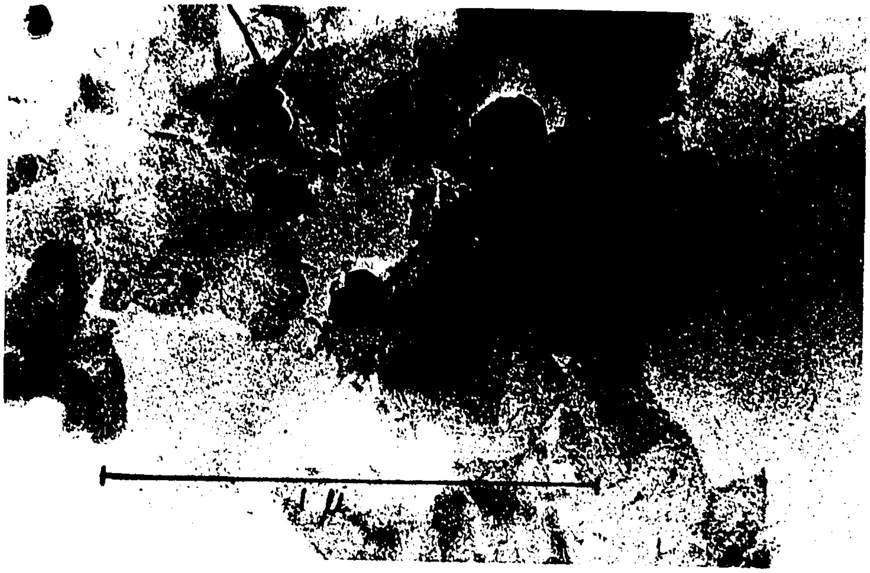
(b) $\frac{OH}{Al}$ = 2.5-clay-O.M.I(pH 2.86)



(c) $\frac{OH}{Al}$ = [illegible].5-clay-O.M.I(pH 7.0)

Fig. [illegible]. Electron micrograph of clay-O.M. complex (x7[illegible])

(c) $\frac{OH}{Al}$ = [illegible] -clay-O.M.I(pH 7.0)



(a) $\frac{OH}{Al}$ = 2.7-clay

(b) $\frac{OH}{Al}$ = 2.7-clay-O.M.I(pH 2.86)

Figure 14. Electron micrographs of clay-O.M. complexes (×70,000)

(a) $\frac{OH}{Al}$ = 2.7-clay (4 weeks after preparation)

(b) $\frac{OH}{Al}$ = 2.7-clay-O.M.I(pH 2.86)

(c) $\frac{OH}{Al}$ = 2.7-clay-O.M.I(pH 7)

Figure 14. Electron micrograph of clay-O.M.I complexes (x70,000)

(c) $\frac{OH}{Al}$ = 2.7-clay-O.M.I(pH 7)

(a) $\frac{\mathrm{OH}}{\mathrm{Fe}}$ = 2.5-clay

(b) $\frac{\mathrm{OH}}{\mathrm{Fe}}$ = 2.5-clay-O.M.I(pH 2.80)

Figure 15. Electron micrographs of clay-O.M. complexes (x70,000)

(a) $\frac{\mathrm{OH}}{\mathrm{Fe}}$ = 2.5-clay (4 weeks after preparation)

(b) $\frac{\mathrm{OH}}{\mathrm{Fe}}$ = 2.5-clay-O.M.I(pH 2.80)

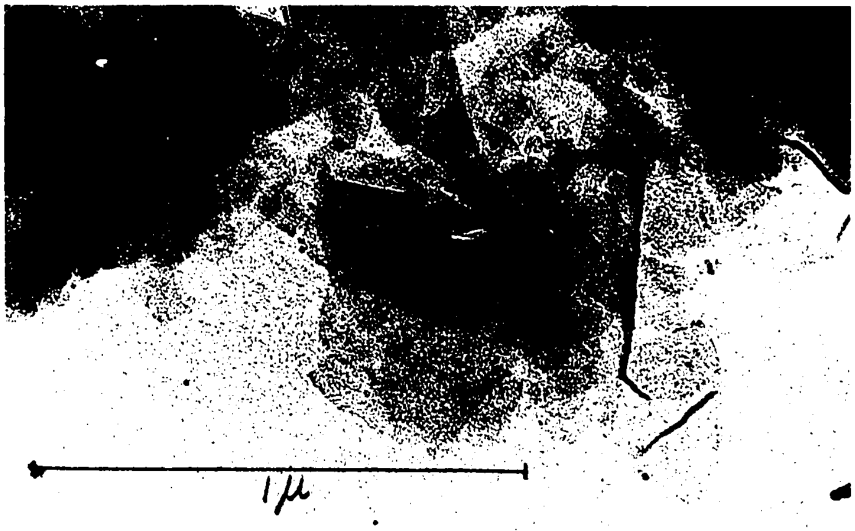


Figure [illegible]. Electron micrograph of clay-[illegible] [illegible] x
(x75,000)
[illegible]-clay-H.[illegible].I(pH [illegible])

IV.2.4. General discussion

Assuming an external surface area of 50 m^2/g for the hydroxy-clays and the Al, Fe saturated clays (Barnhisel 1969; Diamond and Kinter 1956), a value of 50 Å for the average diameter of the organic matter particles (section IV.1.1) and an average molecular weight of 40,000 (Greenland 1965b), the amount of O.M. needed for complete surface (external) coverage, works out to be about 16g O.M./100g clay. This estimate, however, depends on the values used for mean molecular weight and diameter of the O.M. molecule. This maximum amount is of the same order of magnitude or somewhat less than the experimentally obtained values. Higher adsorption may be due to adsorption through extended segments as was suggested by Simha et al (1953) for polymers. Expanded lattice of the Al hydroxy-clays would also have contributed to increased adsorption by increasing edge surface area (Ahlrichs 1962). The "hydroxy Al islands" concentrated near the edges (Dixon and Jackson 1962) and possibly partially exposed, may have provided additional sites of adsorption. In the case of Fe hydroxy-clays, a part of the adsorption may have been due to free ferric hydroxide present as a separate phase.

Flocculation of O.M. by exchangeable Ca, Al has been suggested as possible causes of higher adsorption of O.M. by clays saturated with these ions (Evans and Russell 1959; Martin and Reeve 1960). Polynuclear hydroxy Al ions have been found to be much more efficient than Al^{3+} in coagulating negatively charged colloids (Matijević et al 1961). However, polynuclear hydroxy Al ions on clay surfaces were generally considered non-exchangeable (section II.3). It is therefore not possible to say definitely whether these polynuclear ions, being on clay surfaces, could still exert their flocculating effect.

The pH dependence of adsorption and appreciable adsorption at pH 7 and the results of the desorption experiment lend support to the possible occurrence of hydrogen bonding (of the 3 types, section II.1.2.3.2) and a reaction of the anion penetration type (which is also pH dependent). Electrostatic bridging mechanism may not alone account for all the O.M. adsorbed, especially at pH 7, when the amount of positive charge (both on the hydrous oxide and clay) would be very small.

Results of adsorption studies indicated that O.M. was adsorbed on both edge and planar surface of Al, Fe hydroxy-clays. The adsorption approximately followed the

Langmuir isotherm. Desorption experiments showed that about 15-25% and 20-30% of the adsorbed O.M., respectively for Al and Fe hydroxy-clays was not desorbed by 0.5 N Na_2CO_3 but could be desorbed by 0.5 N NaOH. Adsorption was observed to be pH dependent and noticeable amounts of O.M. were adsorbed by the Al, Fe hydroxy-clays even at pH 7. Electrostatic bridging, anion penetration and hydrogen bonding are suggested as possible mechanisms of bonding of O.M. to the hydroxy-clays.

IV.3. Reactions of organic matter preparations with Al, Fe hydroxy compounds in solution

IV.3.1. pH changes on reaction of hydroxy Al, Fe solutions with model organic compounds and O.M.

pH values of the mixtures of organic anions with Al or Fe hydroxy solutions were greater than the corresponding pH values of the mixtures of Al or Fe hydroxy solutions with distilled water (Tables 8 and 9). The di- and tricarboxylic acid anions were generally more effective than the monocarboxylic acid anions in increasing the pH. These results are in agreement with those reported in the literature (Pockras 1956; Bailar 1956; Gimblett 1963). This increase in pH has been explained on the basis of anion penetration (section II.4).

TABLE 8. pH values of mixtures of hydroxy Al solutions with model organic compounds and organic matter

	pK**	$\frac{OH}{Al}$ = 2.5 solution (pH 4.6)			$\frac{OH}{Al}$ = 2.7 solution (pH 5.3)		
		3 hrs.	1 day	1 week	3 hrs.	1 day	1 week
1. Acetic acid (pH7)*	4.75	6.40	6.37	6.28	6.80	6.82	6.98
2. Citric acid "	3.08 4.74 5.40	7.96	8.27	8.04	8.66	8.72	8.15
3. Tartaric acid "	2.98 4.34	7.25	7.29	7.14	7.43	7.48	7.35
4. Oxalic acid "	1.23 4.19	8.07	8.13	7.72	8.39	8.41	8.08
5. Phthalic acid "	2.89 5.51	6.56	6.59	6.60	7.06	7.03	7.00
6. Salicylic acid"	2.97 13.40	6.98	7.02	7.01	7.12	7.33	7.30
7. E.D.T.A. (pH7)	2.0 2.67 6.16 10.26	6.92	6.95	6.94	7.04	7.08	7.11
8. Pyrogallol (pH7)	9.01 11.64	6.18	5.20	5.00	6.50	5.81	5.06
9. Catechol (pH7)	9.48	6.45	5.65	5.45	6.87	6.09	5.61
10. Distilled water(pH7)	-	4.74	4.70	4.73	5.77	5.68	5.56
11. O.M.I (pH7)	4.6	6.98	6.90	6.88	7.27	7.20	7.07
12. O.M.II(pH7)	5.5	6.90	6.90	6.86	7.26	7.18	7.12
13. O.M.I (pH4.6)	-	5.24	5.50	5.42	-	-	-
14. O.M.II(pH4.6)	-	4.98	5.21	4.98	-	-	-
15. O.M.I (pH5.3)	-	-	-	-	6.22	6.30	6.27
16. O.M.II(pH5.3)	-	-	-	-	6.12	6.10	6.04

Standard error 0.04

*All acids neutralised with NaOH to pH 7.

**pK values of acetic to salicylic acids were obtained from Weast (1968), of E.D.T.A. from Welcher (1958), of pyrogallol and catechol from Rapporport (1967) and of O.M. from Table 1 (section IV.1.1).

TABLE 9. pH values of mixtures of hydroxy Fe solutions with model organic compounds and organic matter.

	$\frac{OH}{Fe}$ = 2.5 solution (pH 2.9)			$\frac{OH}{Fe}$ = 2.7 solution (pH 3.1)		
	3 hrs.	1 day	1 week	3 hrs.	1 day	1 week
1. Acetic acid(pH 7)*	6.27	6.38	6.45	6.39	6.44	6.47
2. Citric acid "	6.72	7.02	7.06	6.90	7.10	7.16
3. Tartaric acid "	6.03	6.53	6.95	6.88	7.00	7.05
4. Oxalic acid "	7.05	7.05	7.18	6.96	7.27	7.42
5. Phthalic acid "	6.00	6.12	6.22	6.58	6.63	6.53
6. Salicylic acid"	4.56	4.98	5.18	5.04	5.06	5.23
7. E.D.T.A. "	7.02	7.01	7.05	7.02	7.09	7.08
8. Pyrogallol "	4.82	4.78	4.60	5.17	5.15	5.10
9. Catechol "	5.00	5.02	4.86	5.81	5.45	5.35
10. Distilled water "	3.19	3.16	3.15	3.65	3.56	3.22
11. O.M.I (pH 7)	6.38	7.05	7.12	7.04	7.15	7.24
12. O.M.II (pH 7)	6.40	6.95	7.05	6.87	6.97	7.08
13. O.M.I (pH 2.9)	2.87	3.10	3.11	-	-	-
14. O.M.II (pH 2.9)	3.10	3.30	3.30	-	-	-
15. O.M.I (pH 3.1)	-	-	-	3.12	3.32	3.37
16. O.M.II (pH 3.1)	-	-	-	3.34	3.56	3.60

Standard error 0.03

*Acids neutralised to pH 7 with NaOH.

E.D.T.A., even though a strong chelator, did not give as high a pH increase as citrate, oxalate or tartrate (Tables 8 and 9). This may be due to several reasons. Firstly, the E.D.T.A. chelates of Al, Fe are not very stable above pH 7 and start breaking down at pH 7–8 (Chaberek and Martell 1959). Hence, the E.D.T.A. anion may not effectively compete with OH ions for coordination positions around Al or Fe at or near this pH. Secondly, the unionised carboxyls in E.D.T.A. ($pK_3 = 6.16$, $pK_4 = 10.26$, Table 8) may have consumed part of the liberated OH ions. Thirdly, the E.D.T.A. anion may have complexed the hydroxy Al or Fe species without displacing OH ions. Scheffer and Ulrich (1960) considered that E.D.T.A. can form complexes with $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$ and $Fe(OH)_3$. Salicylic acid was soluble only when the solutions were warm and crystallised on standing making interpretations of the observed pH values difficult.

Pyrogallol and catechol did not produce appreciable increases in pH values of Al or Fe hydroxy solutions. In fact, on comparison of the pH values of pyrogallol and catechol treatments in Tables 8 and 9 and those in Table 11, it appeared that the reaction of these polyphenols with Al or Fe hydroxy compounds produced more H^+ ions than OH^- ions. The production of H^+ ions may be due to a reaction of Al or Fe hydroxy ions with the polyphenols in a manner similar to

TABLE 10. pH values of mixtures of Al or Fe "hydroxide" with organic matter

	3 hrs.	1 day	1 week
1. O.M.I (pH7) + $Al(OH)_x$ suspension (pH7)	7.60	7.43	7.25
2. O.M.II (pH7) + $Al(OH)_x$ suspension (pH7)	7.47	7.24	7.20
3. O.M.I (pH7) + $Al(OH)_x$ precipitate*	7.40	7.28	7.25
4. O.M.II (pH7) + $Al(OH)_x$ precipitate	7.30	7.25	7.21
5. O.M.I (pH7) + $Fe(OH)_3$ precipitate*	7.25	7.34	7.25
6. O.M.II (pH7) + $Fe(OH)_3$ precipitate	7.18	7.22	7.20

Standard error 0.07

*$Al(OH)_x$, $Fe(OH)_3$ precipitated at pH 7 and freed of supernatant solution by centrifugation and decantation.

TABLE 11. pH values of mixtures of model organic compounds and organic matter with distilled water

	Water at pH 5.30**			Water at pH 3.1**		
	3 hrs.	1 day	1 week	3 hrs.	1 day	1 week
1. Acetic acid (pH7)*	7.19	7.24	7.26	6.19	6.26	6.23
2. Citric acid "	7.26	7.20	7.22	6.63	6.69	6.67
3. Tartaric acid "	7.19	7.17	7.12	6.08	6.04	6.05
4. Oxalic acid "	7.30	7.29	7.32	6.14	6.18	6.21
5. Phthalic acid "	6.95	6.98	6.97	6.30	6.36	6.31
6. Salicylic acid"	7.21	7.26	7.28	5.60	5.64	5.58
7. E.D.T.A. "	6.98	7.04	7.06	6.62	6.71	6.72
8. Pyrogallol "	7.06	6.99	6.93	6.03	5.97	5.85
9. Catechol "	7.09	7.03	6.97	6.17	6.03	5.98
10. O.M.I "	6.92	6.96	7.04	6.08	6.10	6.17
11. O.M.II "	7.08	7.06	7.10	6.16	6.22	6.20

Standard error 0.04

*Acids neutralised with NaOH to pH 7.

**Distilled water adjusted to the respective pH values with HCl.

the formation of a metallo-pyrogallol complex (Mortensen 1963). In the case of pyrogallol and catechol, the solutions turned darker in colour on standing due to atmospheric oxidation (Broadbent 1953). The atmospheric oxidation also could have contributed to lower pH values as it was observed that the pH of alkaline solutions of both pyrogallol and catechol decreased with time (Table 11).

It is known that Fe^{3+} is not precipitated by addition of alkali in the presence of oxalic, citric or tartaric acid (Flaschka and Barnard 1967). Marion and Thomas (1946) observed that the precipitate formed by the addition of alkali to Al^{3+} solutions in the presence of tartrate and citrate contained these anions in the bound form. They also found that the precipitation was completely inhibited when the molar ratio of organic anion was greater than 0.35 and 0.5 for tartrate and citrate respectively. These reports showed the great coordinating and complexing tendency of oxalate, citrate and tartrate for Fe and Al. These anions could effectively compete with OH ions even at high pH values for coordination positions around Fe or Al. Phthalic acid was less efficient than oxalic, tartaric or citric in increasing pH (Tables 8 and 9). Plant (1948) reported that phthalic acid behaved more like monocarboxylic acids than dicarboxylic acids in its "anion penetration" reaction with chromium hydroxide. Whether this was due to steric hindrance or other mechanisms was not known.

Thomas and Vartanian (1935), and Thomas and Whitehead (1931) considered that the effects of dilution and change in activity coefficients were too small to explain the observed increase in pH values. The possibility of buffer action and hydrolysis of the organic anions (salts) contributing to the observed increase in pH values was not considered by the above authors. However, partial contribution by these effects to the observed increase in pH values cannot be overruled.

The combined effect of dilution and hydrolysis was measured by adding distilled water at the same pH as those of the hydroxy Al or Fe hydroxy solutions, to the organic anions or O.M. (Table 11). The effect was studied only at pH values (higher pH values) corresponding to the 2.7 ratio hydroxy solutions (i.e., pH 5.3 and 3.1). Results showed that the pH values obtained with distilled water (Table 11) were lower than (or equal to) those with the hydroxy Al or Fe solutions (Tables 8 and 9), except in the case of acetic acid (only with Al hydroxy solution) and the polyphenols. In the case of acetic acid it may be that the acetate ion did not effectively compete with OH ions at higher pH values and the amount of displaced OH ions was not enough to measurably increase the pH. It should, however, be noted that the hydroxy Al or Fe solutions, though at the same pH as the distilled water used (Table 11), have a higher buffering capacity. In the case of pyrogallol and catechol, reaction of the anion penetration type did not appear to occur.

The pH values of the Al systems generally decreased after 1 day (Table 8), but those of the Fe system increased up to 1 week (Table 9). This indicated that the reaction in the Fe systems was slower and took place for a longer time. The exact reason for the decrease in the pH values of the Al systems after 1 day is not clear but may be due to continued hydrolysis of unreacted Al hydroxy ions, or the slow buffer action of the organic anions or due to microbial activity. The pH values (numerical) in the Fe systems were lower than those of Al systems, possibly due to the lower pH values of the Fe hydroxy solutions.

Both O.M. preparations used in this study showed increase in pH values (Tables 8, 9 and 10), when reacted with Al or Fe hydroxy solutions or their "hydroxides." There was partial flocculation of O.M. in all cases, especially marked at lower pH values. Comparison of pH values in Tables 8 and 9 with the corresponding ones in Table 11 shows that the increase in pH was not solely due to hydrolysis, dilution or (and) buffer action. Further, the increase in pH value, when solutions of the same pH were mixed (treatments 13, 14, 15 and 16 in Tables 8 and 9) showed that the observed effect was due to liberation of OH ions by some reaction of the components involved. Treatments 4, 5 and 6 of Table 10 practically eliminated effects of dilution and hydrolysis. The increase in pH values with O.M. was lower than with citrate, oxalate or tartrate, despite the fact that the O.M. used, had complexing properties (section IV.1.1). The reason for this may be:

(a) the higher equivalent weight of O.M.

(b) all the carboxyl groups may not have been capable or sterically suited for a reaction of the anion penetration type.

(c) the presence of carboxyls and phenolic OH groups of varying strength (not neutralised at pH 7) may have consumed part of the liberated OH ions.

(d) the polyphenolic groups may have produced H^+ ions as discussed for pyrogallol, earlier in this section.

In the case of O.M., too, the reaction in Fe systems was slower than in the Al systems as judged from the increase in pH values.

Similar increase in pH values was reported when O.M. preparations were mixed with partially neutralised Al, Fe solutions (Martin and Reeve 1960; Martin 1960). Schnitzer and Skinner (1963b) reported increases in pH values when a fulvic acid from a Podzol Bh horizon, reacted with gibbsite and goethite at pH values of 3, 5 and 7. The former authors explained the observed increase in pH values as due to the release of OH ions from Al, Fe hydrous oxides by humate anions. The latter authors (Schnitzer and Skinner 1963b) considered the increase in pH values as due to the reaction of "the most acidic carboxyl group" with $Al(OH)_3$ or $Fe(OH)_3$, neutralising one OH group. This reaction may be possible at low pH values but it is unlikely that "the most acidic carboxyl" was still available at pH 7 (where pH increase was observed) for such a neutralisation reaction. However, irrespective of the mechanism involved, the final product is one in which the OH attached to an Al or Fe atom is replaced by a carboxyl group of the O.M. The present author also considers that the observed increase in pH values (in the experiments described here) was due to displacement of OH ions bound to Al or Fe in their hydroxy compounds by carboxyl groups of O.M. However, the possibility of a simple neutralisation reaction is not overruled, especially at low pH values. However, in most natural soils (pH 5-7) the former mechanism may be more plausible than the latter.

Generally, O.M.I gave a greater increase in pH than O.M.II, except in the case of Fe hydroxy solutions at low pH values (treatments 13, 14, 15 and 16, Table 9). The exact reason for this reversal of the order at low pH is not clear. It may be due to the lower pK of O.M.I (Table 1) and hence it would have required a larger amount of OH ions to increase the pH at lower values. The effect was studied only qualitatively. No attempt was made to estimate quantitatively the extent of OH ion release.

IV.3.2 Hydroxyl bound to Al at different pH values in the presence of O.M.

The OH to Al molar ratio at the different pH values in the presence of O.M.I was lower than when no O.M. was present (Table 12). The difference in OH/Al molar ratio above pH 7.6 was within the limits of error of measurement. OH/Al molar ratios above pH 10 were erratic, possibly due to the non-stoichiometry of the reaction of KF (F^-) with aluminate ions (Yuan 1959). Paulson and Murphy (1956) reported a value of 3.6, Watts (1958) a value of 3.9, and Yuan (1959) a value of 3.69 for the number of OH ions per mole of Al produced by F^- ions reacting with AlO_2^- ions. The theoretical value should be 4. A value of 3.8 was obtained in the present investigation.

TABLE 12. Effect of O.M. on the OH/Al ratio of hydroxy Al solution at different pH values

No O.M. added		O.M.I added	
pH	OH/Al	pH	OH/Al
4.52	2.48	4.20	2.31
4.82	2.62	4.32	2.33
5.38	2.64	4.54	2.32
5.68	2.80	5.07	2.50
7.60	2.81	5.35	2.55
8.19	2.85	7.52	2.68
9.02	2.99	9.27	2.91
9.51	3.08	10.32	2.91
10.47	2.94	10.61	2.92
10.81	2.87	10.70	2.90
11.03	2.82	11.04	2.78
		11.32	2.99

Standard error (OH/Al ratio) 0.08

A linear regression of pH on log OH/Al molar ratio (pH 4.2–7.6) gave the following equations:

$Y = 37.46X - 9.47$, ($r = 0.81$) – no O.M. present

$Y = 43.27X - 12.84$ ($r = 0.96$) – O.M.I present

where

Y = pH

X = log OH/Al molar ratio.

Homogeneity of the two regressions was tested as outlined by Steel and Torrie (1960). The regressions were not significantly different.

Results (Table 12), however, indicated that the difference in OH/Al molar ratios with and without O.M., at pH values < 7.6, was greater than the standard error of the mean. This decrease in OH/Al molar ratio was interpreted as due to the functional groups (possibly COOH) of organic matter occupying some of the coordination positions around Al atoms at low pH values but being progressively displaced by OH ions at higher pH values. It was not possible to decide the exact pH at which the O.M. was completely displaced by OH ions, due to the non sensitivity of the method at higher pH values. The low values for the reduction in OH/Al molar ratio was probably due to the very low amount of O.M.I used (0.007 meq COOH to 0.2 meq Al). Higher amounts of O.M. could not be used due to difficulty in detecting the end point. Lower amounts of Al were tried but it was found difficult to obtain consistent values for duplicates. It was not possible to use the method for the Fe system due to difficulty in detecting the end point.

IV.3.3. Infra-red spectra of Al or Fe hydroxy compounds-O.M. complexes

The changes in the spectra of O.M.I and O.M.II on reaction with hydroxy Al or Fe compounds were similar. The shifts in the bands were very similar for hydroxy Al and Fe-O.M. complexes. The spectra of O.M.I was described and discussed in section IV.1.1 (Figure 4).

The principal changes in the I.R. spectra occurred in the 1800 to 1200 cm^{-1} region (Figure 17). On reaction with Al or Fe hydroxy solution or Al^{3+} or Fe^{3+} solution, the shoulder at 1720 cm^{-1} in the original acid O.M.I (Figure 17d) completely disappeared (Figure 17a, b, c) and the peak at 1630 cm^{-1} was slightly increased in intensity and broadened extending from 1630-1600 cm^{-1}. Disappearance of the 1720 cm^{-1} shoulder indicated that the carboxyl groups were involved in complex formation. The disappearance may not be entirely due to ionisation, since the spectrum of O.M.I neutralised with NaOH to the corresponding pH values (Figure 17e, f) still showed a residual shoulder (though

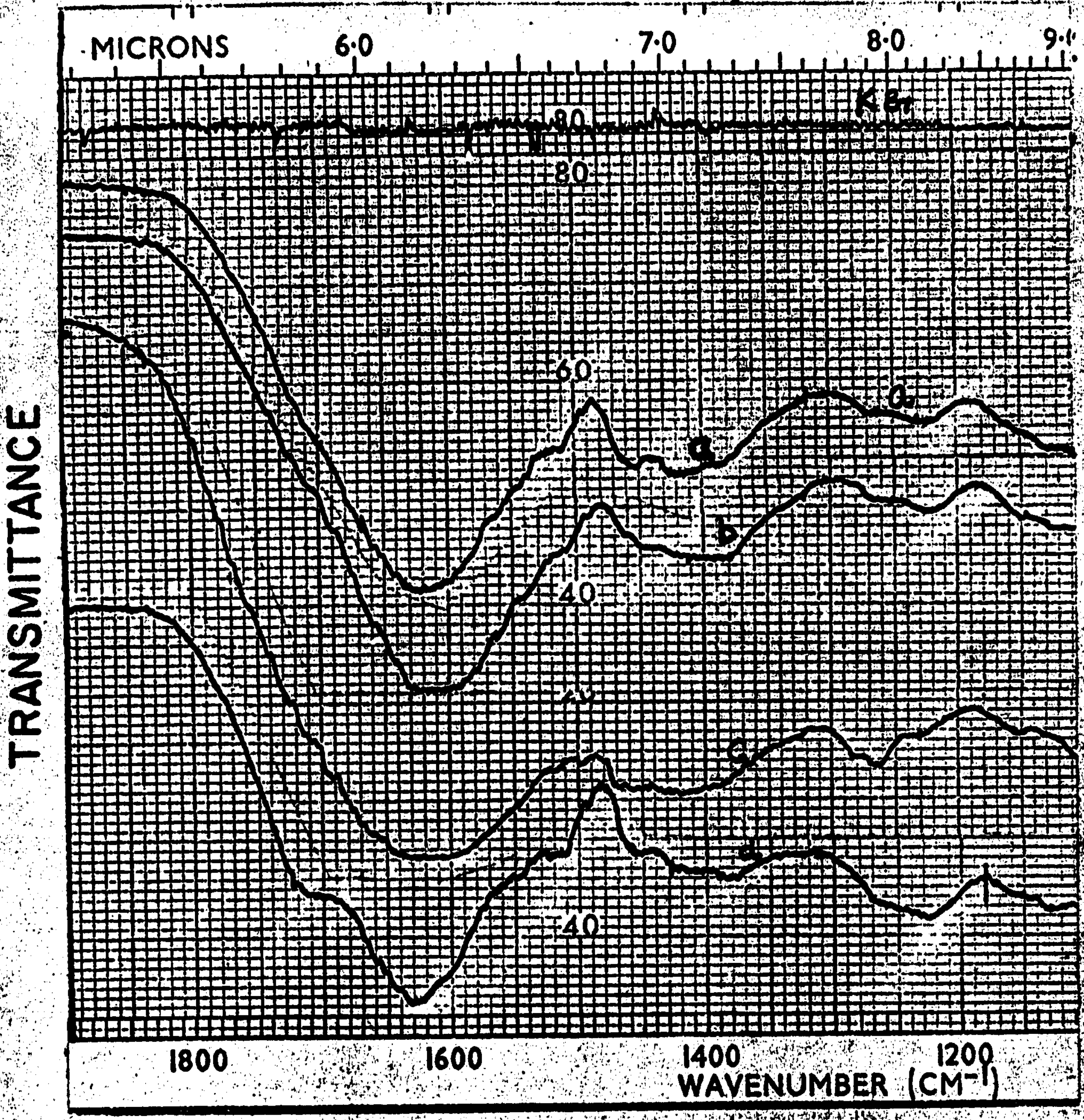


Figure 17. Infra-red spectra of O.M.I-hydroxy Al complexes.

(a) O.M.I + OH/Al = 2.7 solution (pH 5.3)
(b) O.M.I + OH/Al = 2.5 solution (pH 4.6)
(c) O.M.I + Al^{3+} (pH 3.0)
(d) O.M.I (2.86)

(original recordings are available on file at Soil Science Department, Macdonald College)

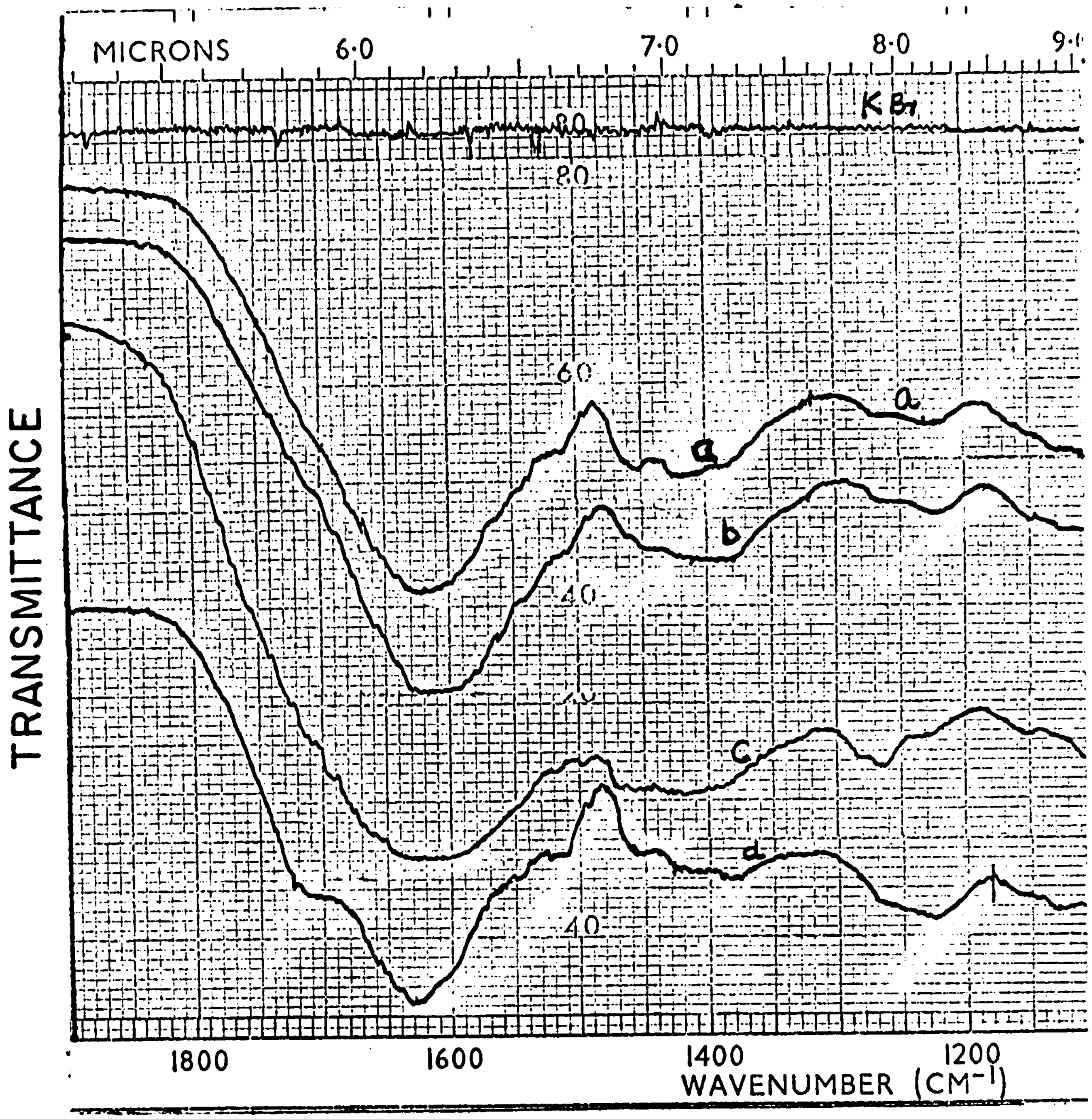


Figure 17. Infra-red spectra of O.M.I-hydroxy Al complexes.

(a) O.M.I + OH/Al = 2.7 solution (pH 5.3)

(b) O.M.I + OH/Al = 2.5 solution (pH 4.6)

(c) O.M.I + Al^{3+} (pH 3.0)

(d) O.M.I (2.86)

(original recordings are available on file at Soil Science Department, Macdonald College)

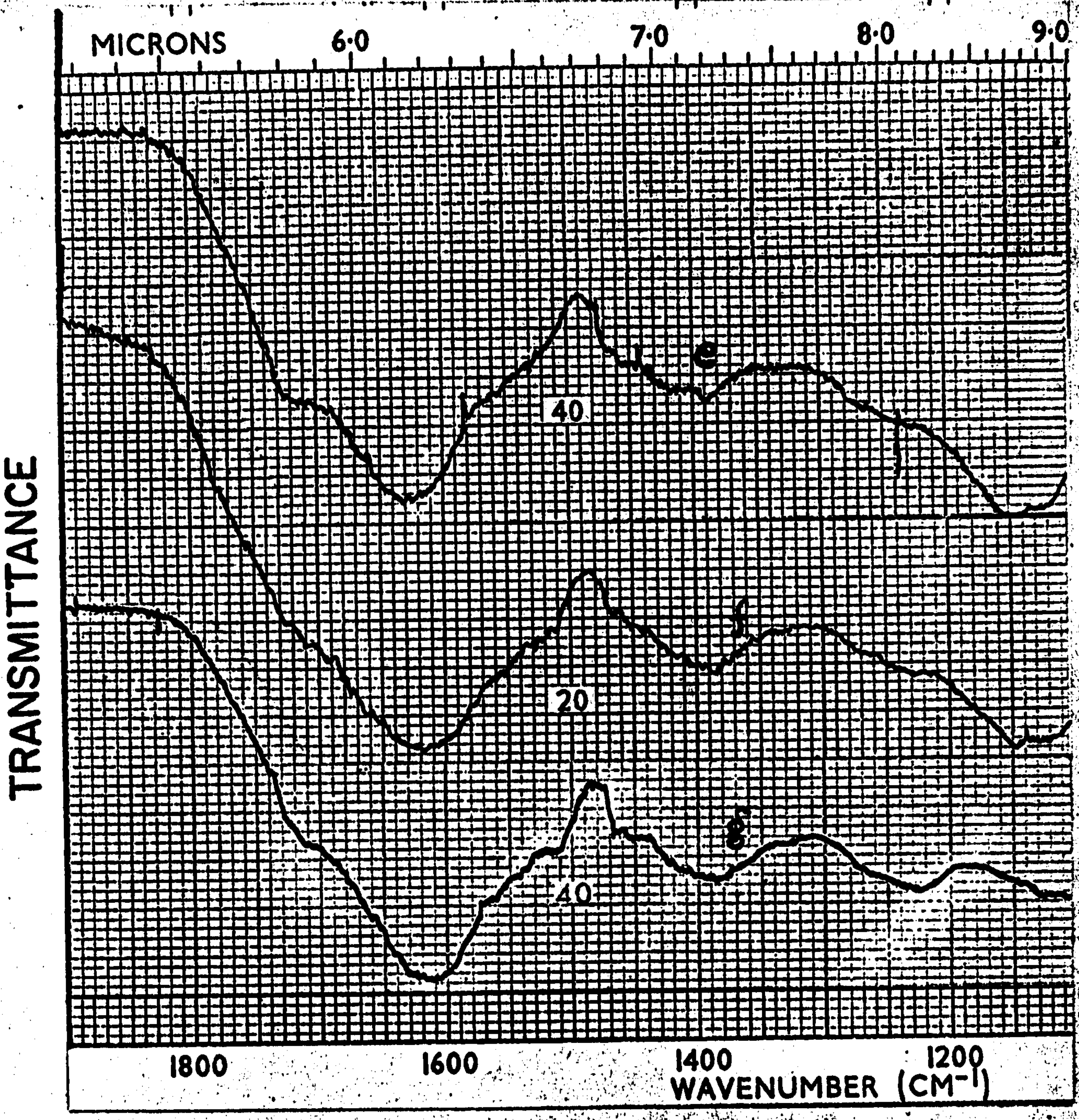


Figure 17. Infra-red spectra of O.M.I-hydroxy Al complexes.

(e) O.M.I neutralised to pH 4.6

(f) O.M.I neutralised to pH 5.3

(g) O.M.I neutralised to pH 7.0

(original recordings are available on file at Soil Science Department, Macdonald College)

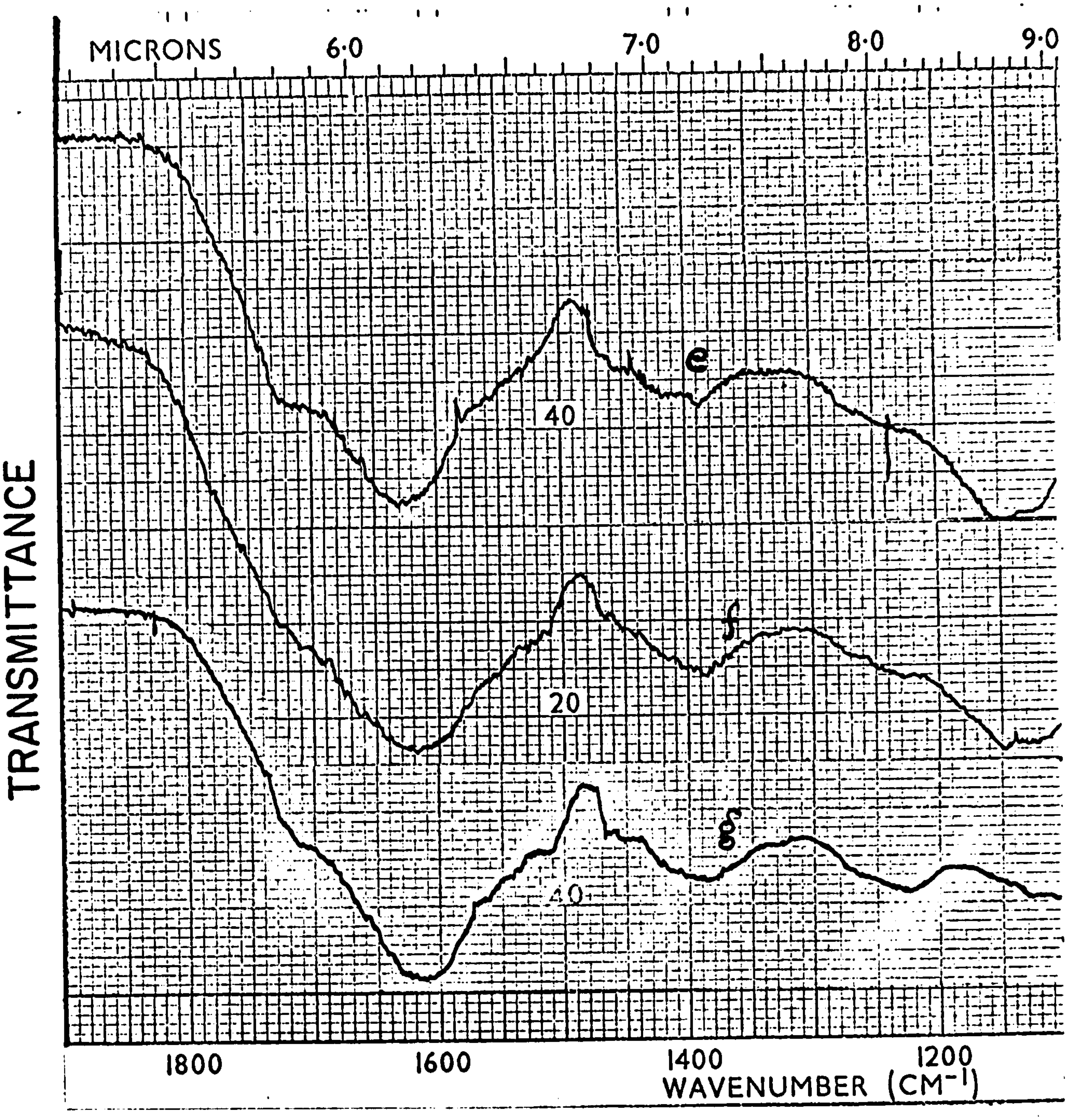


Figure 17. Infra-red spectra of O.M.I-hydroxy Al complexes.

(e) O.M.I neutralised to pH 4.6

(f) O.M.I neutralised to pH 5.3

(g) O.M.I neutralised to pH 7.0

(original recordings are available on file at Soil Science Department, Macdonald College)

reduced in intensity, at 1720 cm^{-1}). The spectrum of the neutralised (pH 7) O.M.I showed a weak but observable residual shoulder at 1710 cm^{-1} (Figure 17g), which was absent in the complexes with hydroxy Al or Fe compounds or Al^{3+} or Fe^{3+} ions. This was possibly due to unionized weak COOH or ketonic C = O groups (Theng and Posner 1967). If the residual shoulder was due to ketonic C = O groups, then it would have shifted (or disappeared) when the C = O coordinated to Al or Fe atom (Parfitt and Mortland 1968). Schnitzer and Skinner (1963a, 1964) interpreted the shift (or disappearance) of the 1720 cm^{-1} band as due to "ionisation of carboxylic acid groups due to the formation of electrovalent metal carboxylate bonds."

Nakamoto (1963) has described the following carbonyl stretching band positions for the unionized, ionized and coordinated carboxyl groups:

unionized - 1750-1700 cm^{-1}
ionized - 1630-1575 cm^{-1}
coordinated - 1650-1590 cm^{-1}

There is some overlap between the frequencies of coordinated and ionised carboxyls. The exact position of the band for a coordinated carboxyl depends on the relative ionic or covalent character of the metal-carboxyl coordinate bond.

Martell and Calvin (1952) stated that the coordinate bond could be covalent, ionic or intermediate in character.

These band positions (i.e., mentioned above) were used to distinguish unreacted carboxylic acid groups from coordinated carboxyl groups in E.D.T.A. and tartaric acid metal chelates or complexes (Busch and Bailar 1953; Sawyer and Paulson 1957; Sawyer and McKinnie 1960; Kirschner and Kiesling 1960). These workers considered that a band in the 1550-1610 cm^{-1} range indicated that the metal carboxyl coordinate bond was primarily ionic and a band in the 1625-1650 cm^{-1} was indicative of primarily covalent character. Sawyer and McKinnie (1960) considered that in Al chelates of E.D.T.A., the metal-carboxyl coordinate bond was as ionic as it was for sodium acetate.

When tartaric acid was reacted with hydroxy Al or Fe solution, the band at 1740 cm^{-1} (COOH, Figure 18c) shifted to 1640-1630 cm^{-1} (Figure 18a, b) as compared with the 1620 cm^{-1} band in sodium tartrate (Figure 18f). Similar shift was observed in copper tartrate and was taken as evidence of formation of coordinate bonds between carboxyl groups and copper atom (Kirschner and Kiesling 1960). Tartaric acid is known to form complexes with Al and Fe (Flaschka and Barnard 1967) and therefore the above shift

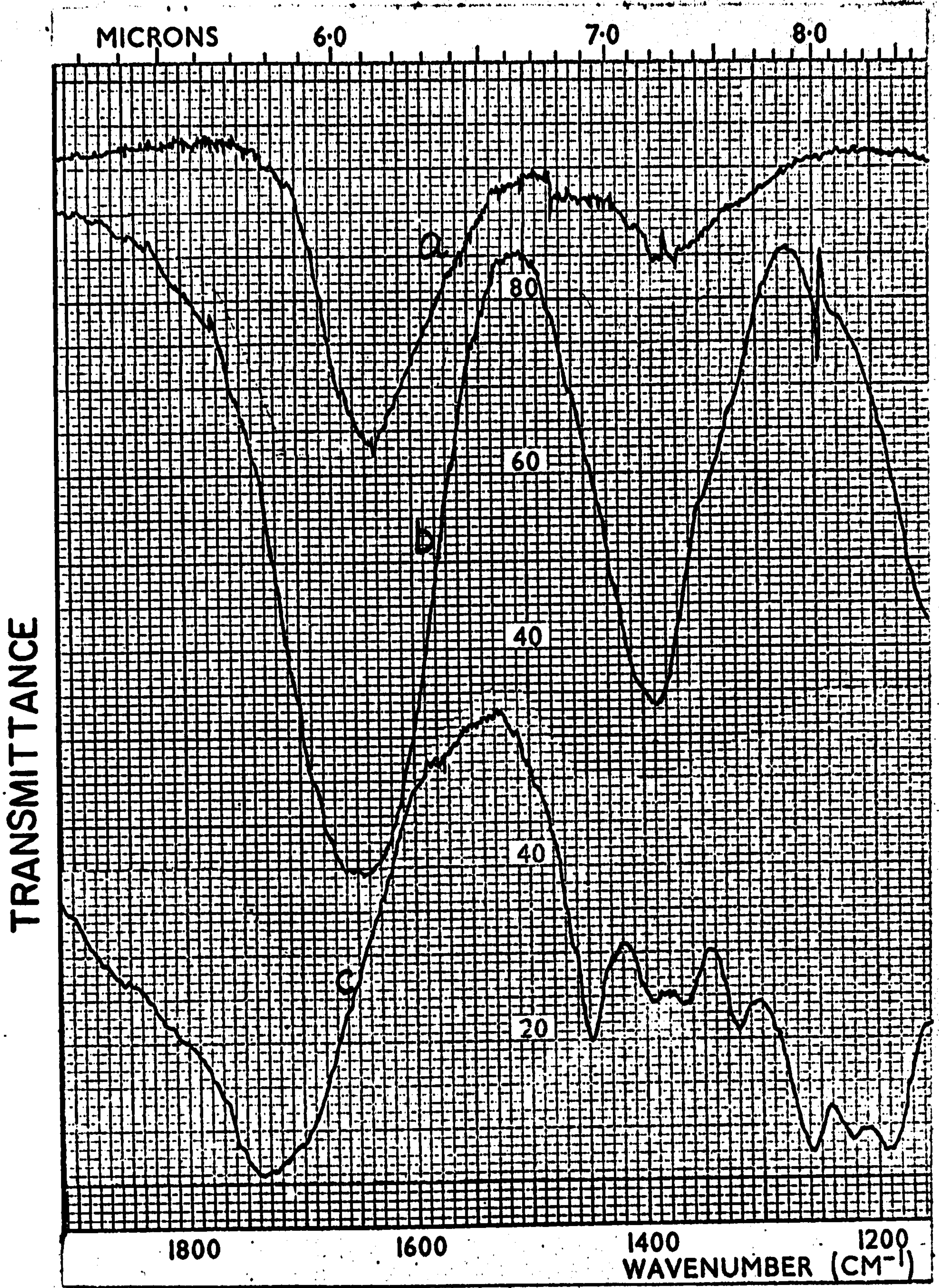


Figure 18. Infra-red spectra of tartaric acid-hydroxy Al or Fe compound complexes.
(a) Tartaric acid + OH/Fe = 2.5 solution (pH 2.9)
(b) Tartaric acid + OH/Al = 2.5 solution (pH 4.6)
(c) Tartaric acid
(original recordings are available on file at Soil Science Department, Macdonald College)

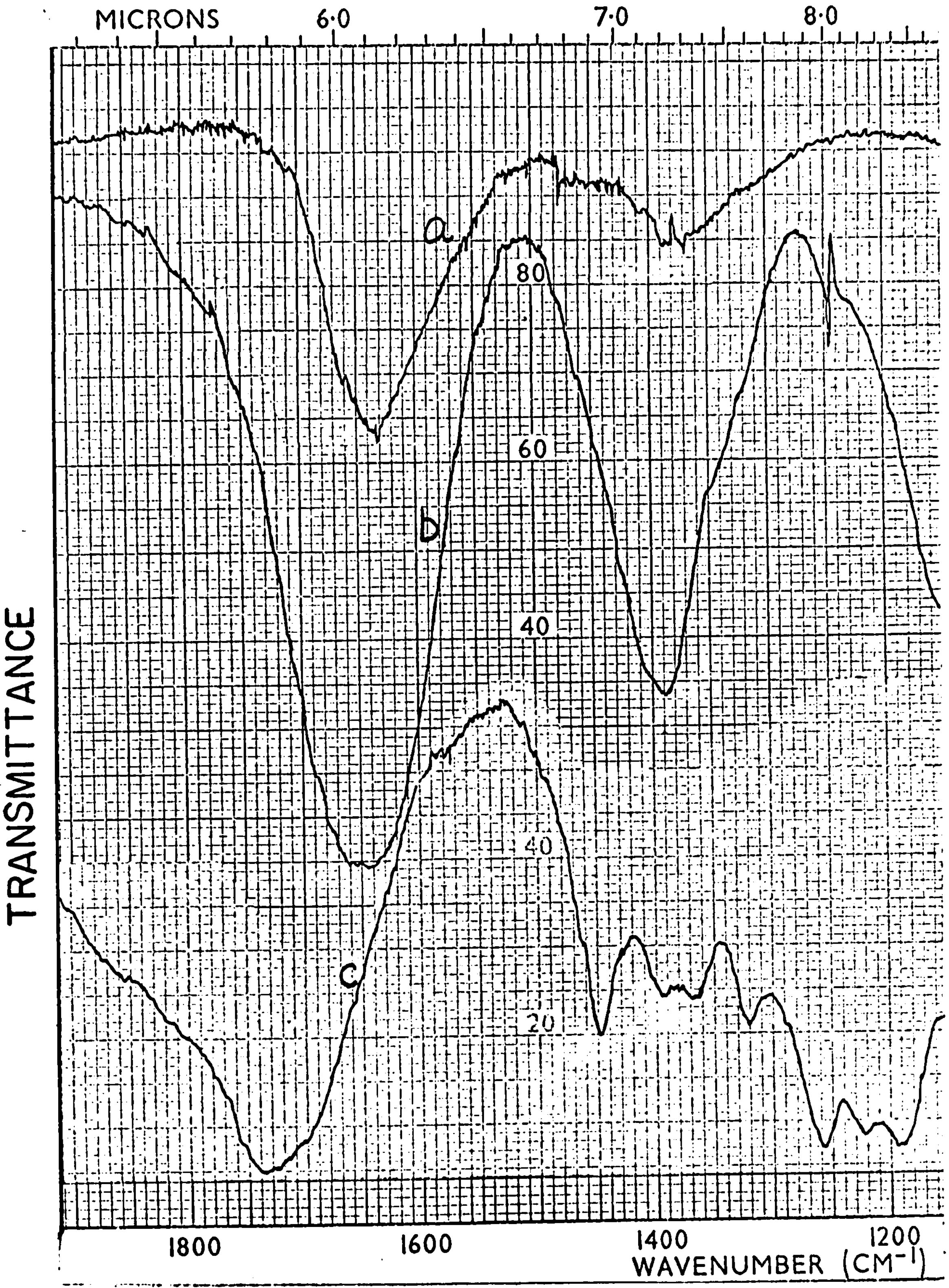


Figure 18. Infra-red spectra of tartaric acid-hydroxy Al or Fe compound complexes.
(a) Tartaric acid + OH/Fe = 2.5 solution (pH 2.9)
(b) Tartaric acid + OH/Al = 2.5 solution (pH 4.6)
(c) Tartaric acid
(original recordings are available on file at Soil Science Department, Macdonald College.)

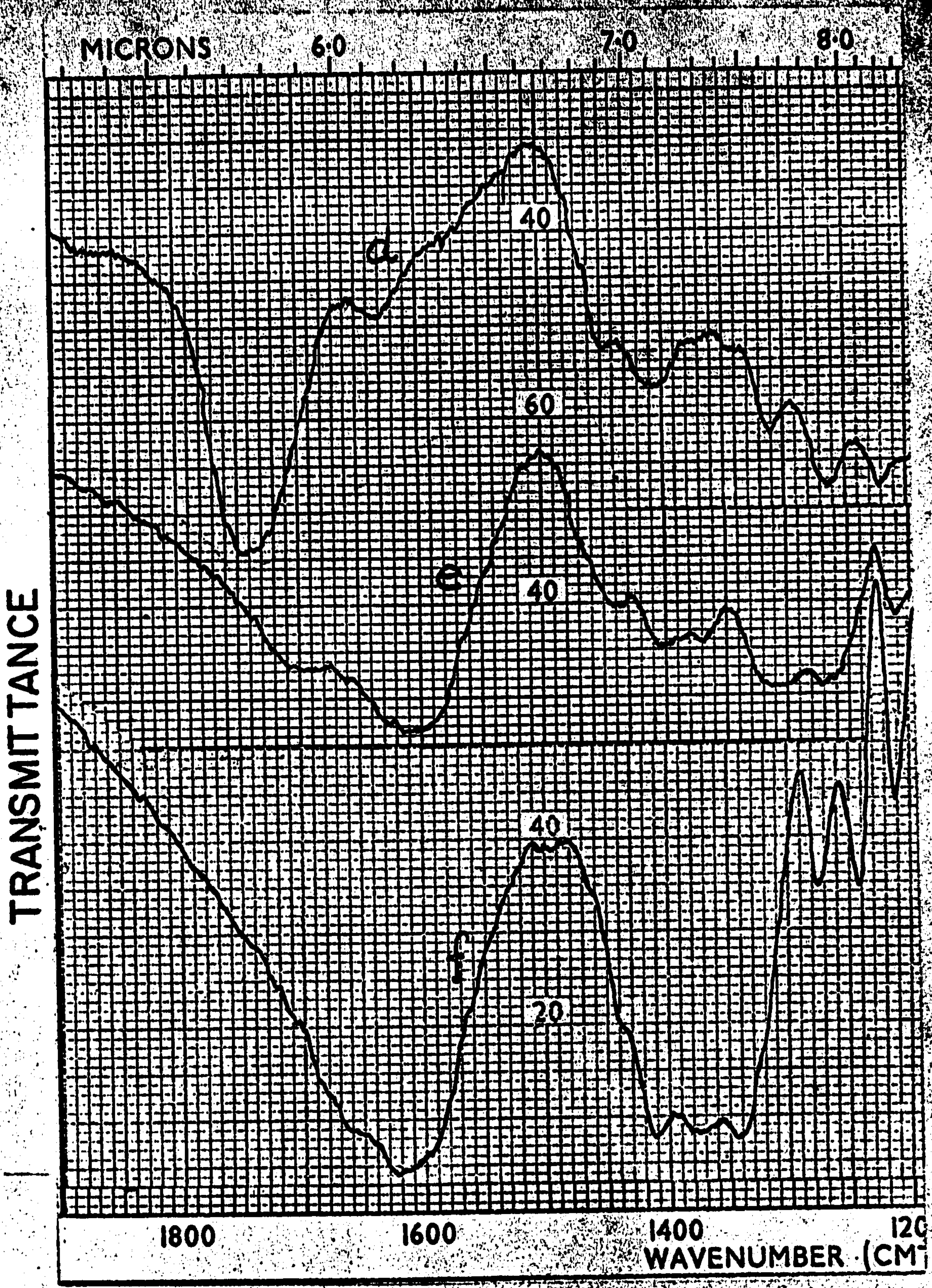


Figure 18. Infra-red spectra of tartaric acid-hydroxy Al or Fe compound complexes.
(d) Tartaric acid neutralised to pH 2.9
(e) Tartaric acid neutralised to pH 4.6
(f) Sodium tartrate
(original recordings are available on file at Soil Science Department, Macdonald College)

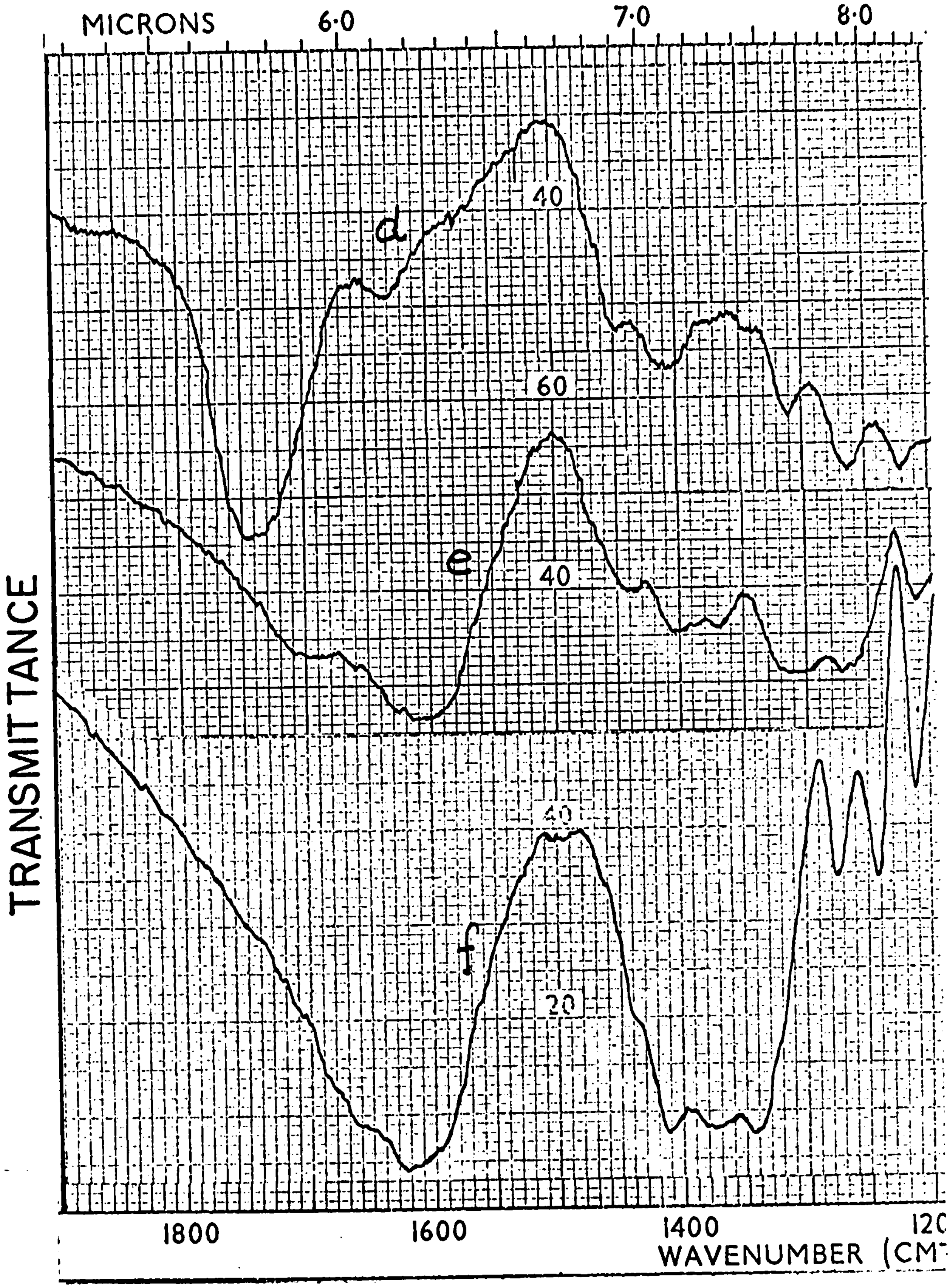


Figure 18. Infra-red spectra of tartaric acid-hydroxy Al or Fe compound complexes.
(d) Tartaric acid neutralised to pH 2.9
(e) Tartaric acid neutralised to pH 4.6
(f) Sodium tartrate
(original recordings are available on file at Soil Science Department, Macdonald College.)

(Figure 18) could be interpreted as due to the coordination of carboxyls to Al or Fe atom. Tartaric acid neutralized with NaOH to pH 4.6 and 2.9 (the respective pH values of reaction with Al or Fe hydroxy solutions) did not show a complete shift in the 1740 cm^{-1} band (Figure 18d, e).

Thus it appeared that the shift (or disappearance) of the 1720 cm^{-1} shoulder and the broadening of the peak at 1630 cm^{-1} was not entirely due to ionisation of carboxyl groups. Coordination of the carboxyls to Al or Fe atoms in the hydroxy compounds may also have been involved but the coordinate bond so formed appeared to be predominantly ionic in character. Such a situation would explain the broadening of the 1630 cm^{-1} band as was observed here and also reported by others (Schnitzer and Skinner 1963a, 1964). It is not essential that the carboxyl group be ionised before it is coordinated to a metal atom. Titanium chelate of E.D.T.A. has been prepared by the action of E.D.T.A. (acid) on TiO_2 (Sawyer and McKinnie 1960). O.M. neutralised to pH 7 and then reacted with the hydroxy solutions gave similar spectra, but in this case almost complete ionization of carboxyls would have occurred before reaction.

The intensity of the 1400 cm^{-1} (Figure 17d) of O.M.I increased slightly on reaction with hydroxy Al or Fe compounds (Figure 17a, b, c). This also indicated that carboxyl groups were involved in the reaction. The band in the 1200 cm^{-1} region was not clear enough to observe any changes.

There was a slight decrease in the intensity but no shift of the bands at 2930 and 2850 cm^{-1} of O.M.I, after reaction with the hydroxy Al or Fe compounds. A shift in the 2800-3000 cm^{-1} band (C-H stretching in CH_2) has been considered as evidence of chelate formation in the case of E.D.T.A. (Sawyer and McKinnie 1960). It was not possible to decide the exact significance of the decrease in intensity of the bands at 2930 and 2580 cm^{-1} of O.M.I.

The I.R. spectrum of $Al(OH)_3$ or $Fe(OH)_3$ (Figure 19) did not show any absorption band in the 1800-1200 cm^{-1} region, which would interfere with the interpretations discussed here.

Thus the I.R. spectra of the O.M. complexes with Al or Fe hydroxy compounds have been interpreted as indicating the formation of both purely ionic and coordinate bonds between carboxyls of O.M. and metal atoms. The coordinate bonds appeared to be predominantly ionic in character.

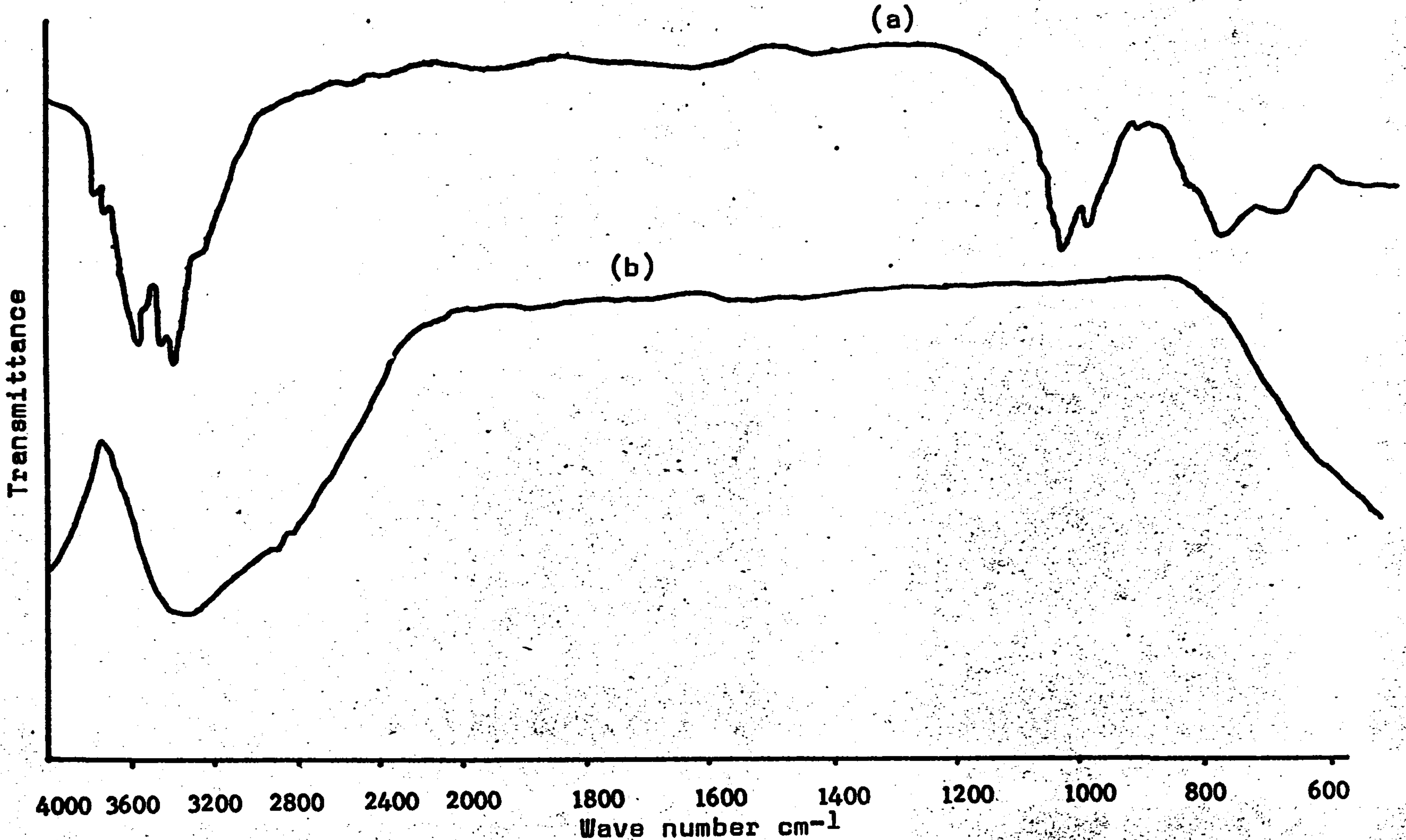


Figure 19. Infra red spectra of $Al(OH)_3$ and $Fe(OH)_3$
(a) $Al(OH)_3$
(b) $Fe(OH)_3$

(original recordings are available on file at Soil Science Department, Macdonald College)

IV.4. Reactions of organic matter with hydroxy Al or Fe compounds on clay surfaces

IV.4.1 pH changes on reaction of O.M. with Al or Fe hydrous oxide coated montmorillonite

Increases in pH values were observed when O.M. preparations were mixed with the hydrous oxide coated clays (Table 13). The explanation for the increase in pH values is the same as the one discussed in section IV.3.1. The effects of dilution and hydrolysis were almost eliminated in these measurements, since the supernatant liquid (in the clay suspension) was removed by centrifugation prior to mixing.

The increase in pH was, however, lower than in the case of Al, Fe hydroxy solutions (Tables 8, 9). This was possibly due to buffering action of the clay. Further, the interlayer hydrous oxide was not available for reaction with the O.M. (section IV.2.3). Since the hydrous oxide was precipitated onto the clay surface, steric effects may have reduced the anion penetration to a greater extent than in the case of hydroxy solutions. The drop in pH value with time was greater in the clay systems than in the case of hydroxy solutions. This again could be attributed to buffering action of the clay. The general trend in the increase in pH values (Table 13) showed that replacement of

TABLE 13. pH values of mixtures of Al, Fe hydroxy-clays with organic matter

	$\frac{OH}{Al}$ = 2.5 ratio clay (pH 4.5)			$\frac{OH}{Al}$ = 2.7 ratio clay (pH 5.2)		
	3 hrs.	1 day	1 week	3 hrs.	1 day	1 week
Al hydroxy-clay systems						
1. O.M.I (pH 7)	6.96	6.95	6.88	7.22	7.14	7.05
2. O.M.II (pH 7)	6.90	6.85	6.82	7.11	7.08	7.00
3. O.M.I (pH 4.5)	5.18	5.08	4.86	-	-	-
4. O.M.II (pH 4.5)	4.95	4.80	4.68	-	-	-
5. O.M.I (pH 5.2)	-	-	-	5.90	5.82	5.69
6. O.M.II (pH 5.2)	-	-	-	5.78	5.66	5.54
Fe hydroxy-clay systems	$\frac{OH}{Fe}$ = 2.5 ratio clay (pH 3.3)			$\frac{OH}{Fe}$ = 2.7 ratio clay (pH 3.5)		
	3 hrs.	1 day	1 week	3 hrs.	1 day	1 week
7. O.M.I (pH 7)	6.25	6.10	6.05	6.38	6.20	6.12
8. O.M.II (pH 7)	6.12	6.15	6.00	6.35	6.22	6.08
9. O.M.I (pH 3.3)	3.38	3.36	3.39	-	-	-
10. O.M.II (pH 3.3)	3.40	3.37	3.35	-	-	-
11. O.M.I (pH 3.5)	-	-	-	3.68	3.70	3.62
12. O.M.II (pH 3.5)	-	-	-	3.65	3.62	3.65

Standard error 0.08

OH groups in hydrous oxide plastered on clay surface by carboxyl groups of O.M. was possible under the conditions used in the experiment.

IV.4.2. I.R. spectra of hydroly Al or Fe-montmorillonite-O.M. complexes.

The changes in the 1800-1200 cm^{-1} region were very much less distinct (Figure 20) than those observed in the Al or Fe hydroxy compound-O.M.I complexes. Hydroxy-montmorillonite clay itself showed a small peak at 1630 cm^{-1} (Figure 20c, d) due to adsorbed water (Grim 1953). Al and Fe systems gave similar spectra. The shoulder at 1720 cm^{-1} of O.M.I was very much reduced in intensity and a very weak shoulder was identifiable at 1710 cm^{-1} (Figure 20,a,b) in the spectra of the clay-O.M.I complexes. The band at 1630 cm^{-1} was very much stronger (in intensity) and there was not much broadening. The band stayed at 1635-1630 cm^{-1}. Absorption band in the 1400 cm^{-1} region was visible but not very prominent (Figure 20a, b).

The lack of clear cut shift in the absorption bands and the interfering band of the clay adsorbed water make definite conclusions difficult. However, the trend in decrease in intensity of the 1720 cm^{-1} shoulder and increase in intensity of the 1630 cm^{-1} band suggested that reactions

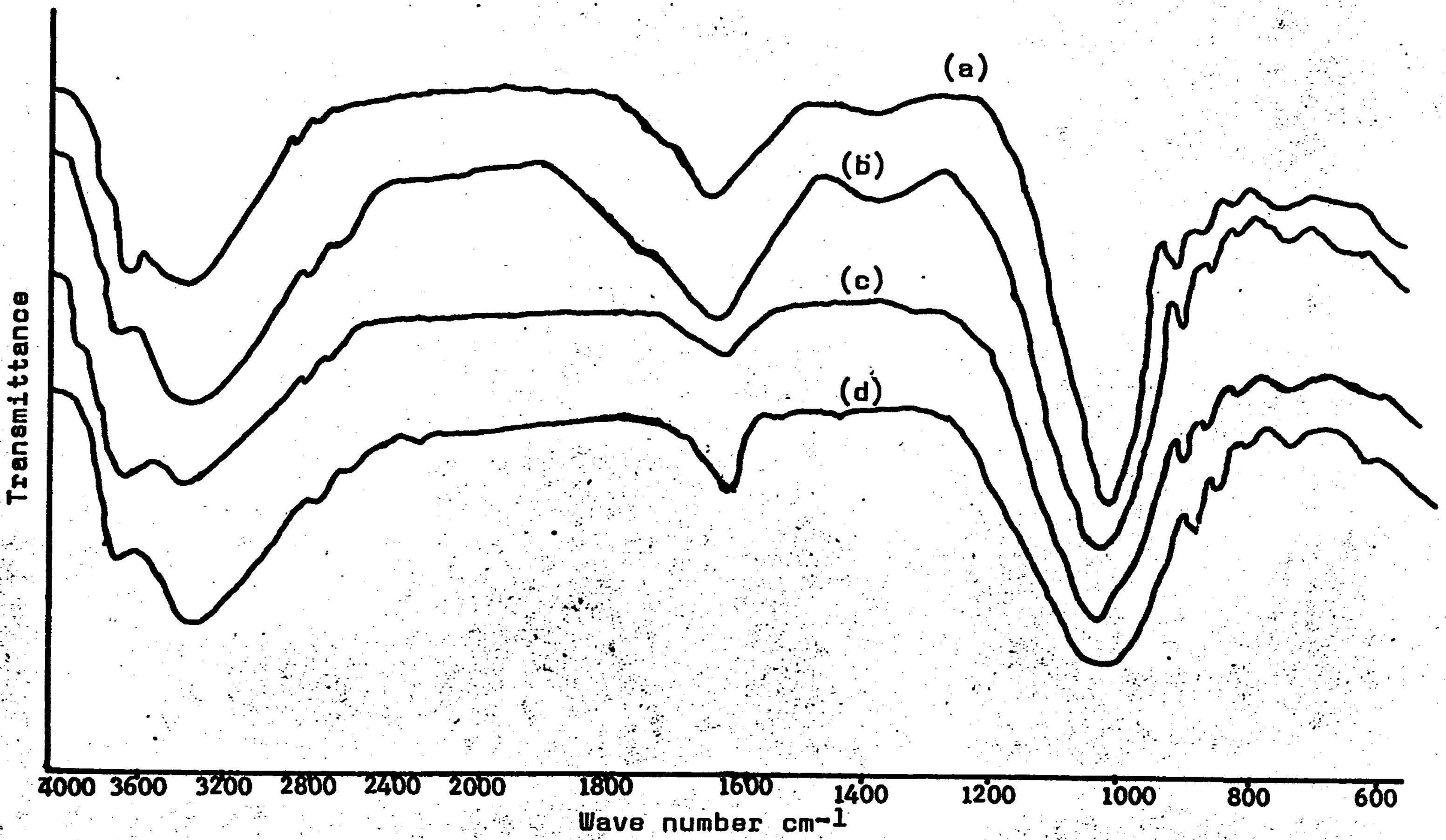


Figure 20. Infra-red spectra of hydroxy-clay-O.M. complexes
(a) OH/Al = 2.5 clay - O.M.I (pH 4.5)
(b) OH/Fe = 2.5 clay - O.M.I (pH 3.3)
(c) OH/Al = 2.5 clay; (d) OH/Fe = 2.5 clay
(original recordings are available on file at Soil Science Department, Macdonald College.)

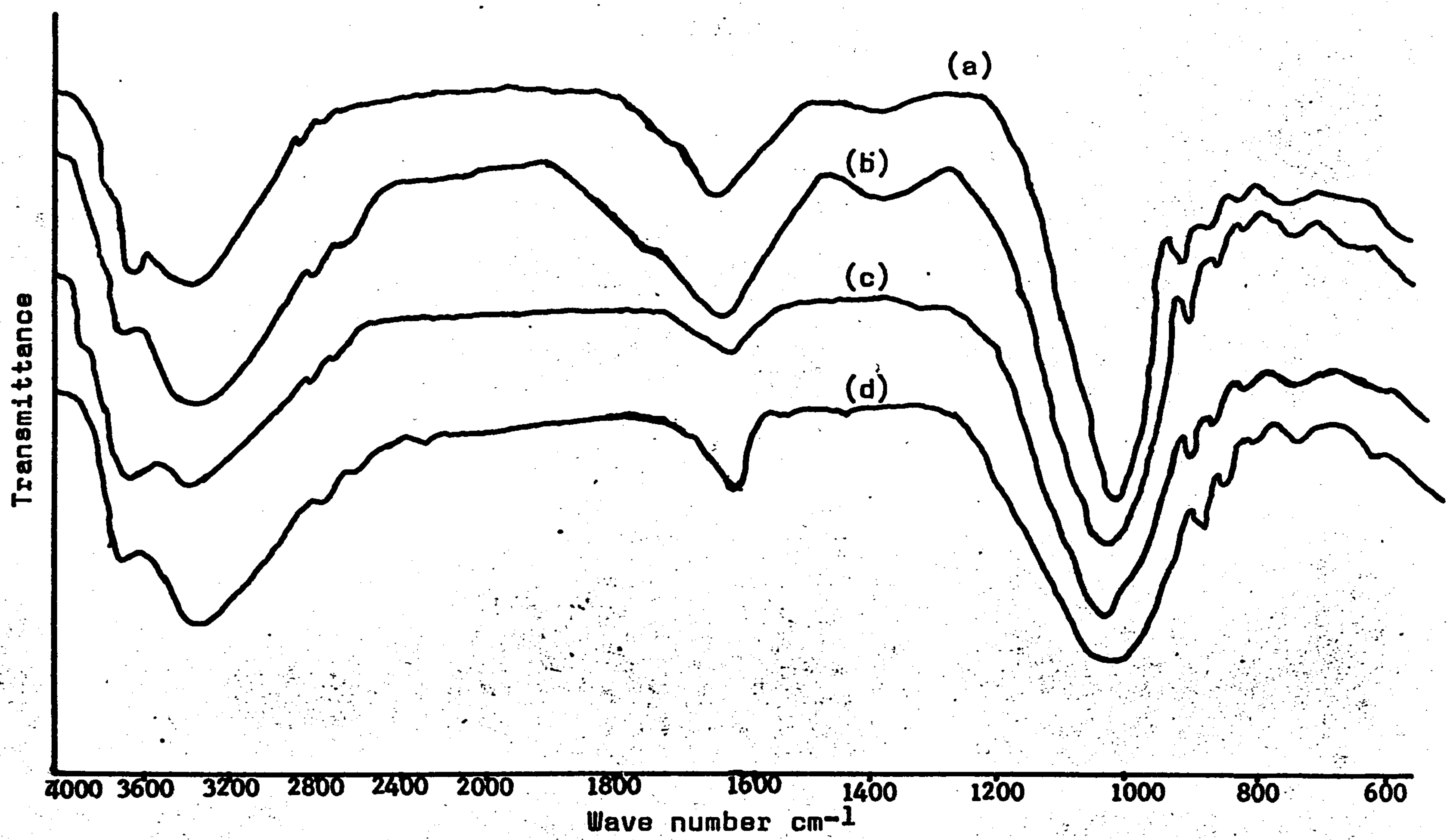


Figure 20. Infra-red spectra of hydroxy-clay-O.M. complexes
(a) OH/Al = 2.5 clay - O.M.I (pH 4.5)
(b) OH/Fe = 2.5 clay - O.M.I (pH 3.3)
(c) OH/Al = 2.5 clay; (d) OH/Fe = 2.5 clay
(original recordings are available on file at Soil Science Department, Macdonald College.)

of O.M.I similar to those discussed in the case of Al or Fe hydroxy compounds in solution (i.e., ionisation and coordination, section IV.3.3) took place with the Al or Fe hydrous oxides on the clay surface. It should be pointed out that the reduction in intensity of the 1720 cm^{-1} band may have been partly due to the small amount of O.M.I in the clay-O.M. complex (this was partly compensated by taking an increased weight of the complex for KBr disc preparation). Presence of a residual shoulder at 1710 cm^{-1} in the complexes indicated that not all carboxyls of the adsorbed O.M. reacted with or bonded to the hydrous oxide on the clay surface or to the clay itself. Thus there still remained some unionised or uncoordinated carboxylic acid groups. The possible steric hindrance due to the spatial distribution of carboxyls in the O.M. may have been responsible for this behaviour. Untreated sodium bentonite did not adsorb enough O.M. to produce observable differences in the spectrum.

IV.4.3. General discussion

The results discussed in sections IV.3 and IV.4 showed that the carboxyl groups in O.M. could displace OH ions bound to Al or Fe hydroxy compounds occurring both free in solution and on clay surfaces, at low pH values. Organic matter thus bonded was gradually released at higher pH values by a reversal of the reaction. It was not possible to determine the exact pH at which the O.M. was completely displaced by OH ions, but it appeared to be higher than 7.5. The results of the desorption experiment (section IV.2.1) and results of other workers (Schwertmann 1966; Schwertmann et al 1968; Sen 1960) showed that O.M. could be retained by hydrous oxides at still higher pH values. The role of phenolic groups and N containing groups in bonding O.M. to hydroxy Al or Fe compounds was not examined. Mechanisms involving these groups may also be responsible for retention of O.M. at higher pH values.

It was not possible to evaluate the exact contribution of the proposed (anion penetration) mechanism because anion penetration, electrostatic bonding and hydrogen bonding tend to behave the same way with increase in pH. The structures of the complexes formed may be similar to those proposed for chromium hydroxide-organic anion complexes (Bailar 1956; section II.4). It was not possible to say whether it was one or two or more carboxyls per Al or Fe atom that were involved in the bonding. All carboxyls in the O.M. did not react with hydrous oxide coated clays possibly due to steric hindrance. From a study of the "anion penetration" reaction with model organic compounds, it appeared that chelating groups (similar to tartaric, oxalic or citric acid) if present in the O.M. would enhance such a reaction.

Thus, based on the evidence so far presented, it is suggested that a part of the O.M. adsorbed by Al or Fe hydroxy-montmorillonite was bonded to hydroxy Al or Fe compounds through the carboxyl groups. The bonding took place by replacement of OH groups coordinated to Al or Fe atoms in the hydrous oxides. The occurrence of such a mechanism does not preclude the operation of other mechanisms.

IV.5. Effect of O.M. on the formation of X-ray crystalline aluminum hydroxide

The ratios of organic carbon (O.M.I) to Al in the mixtures used in experiment IX were 0, 1.52, 2.51, 3.81 and 7.61. X-ray diffraction showed a sharp peak at 4.85 Å, characteristic of gibbsite (Brindley 1951), in the control treatment (no O.M. added), at the end of 2 weeks. No diffraction peaks were obtained in the other treatments at this time. A small broad peak was observable only in the treatment with C:Al ratio of 1.52 at 4 weeks time (Figure 21). On aging, the peak increased in intensity but was still broad and diffuse. No X-ray diffraction peak was observed in treatments with higher C:Al ratios, even after 3 months

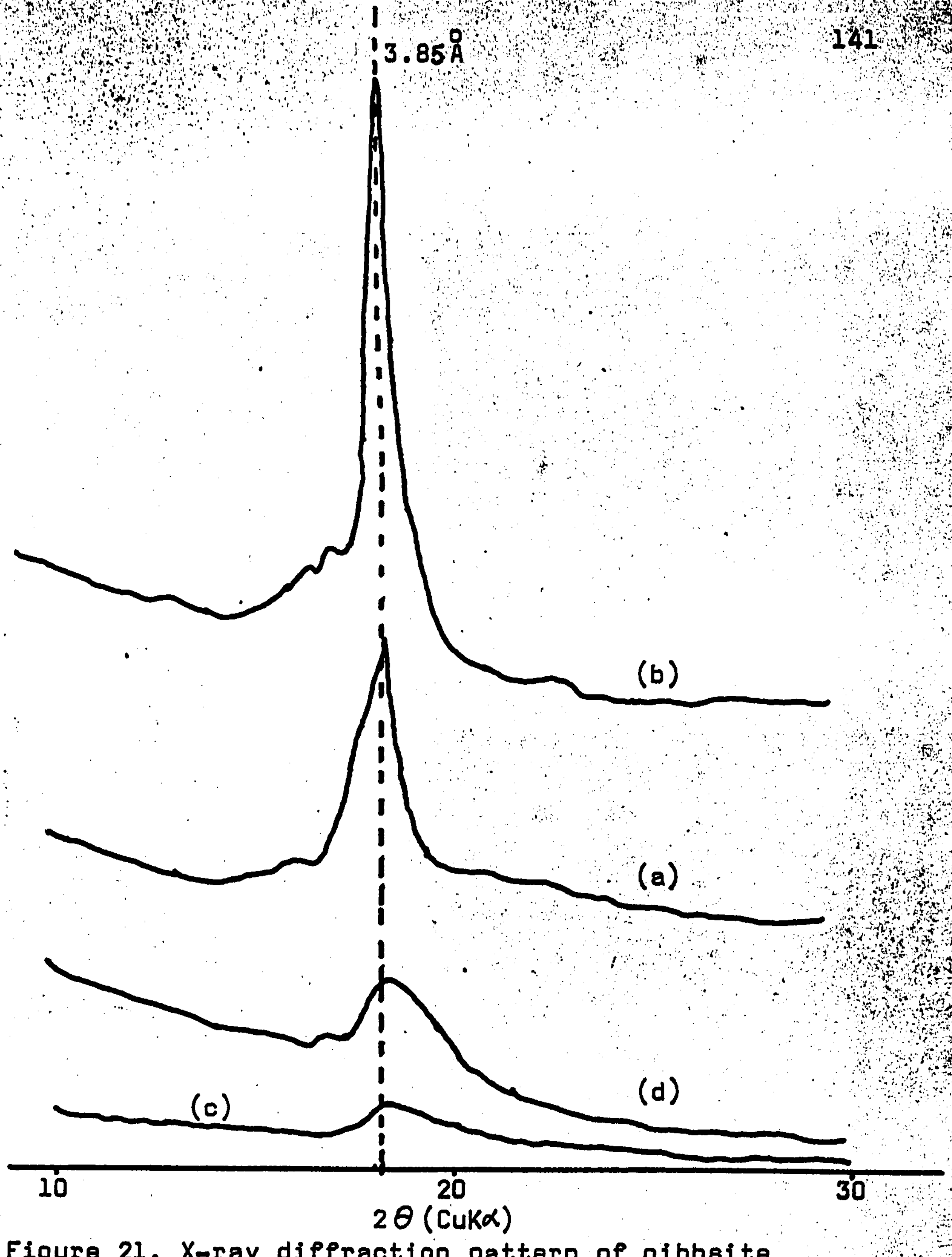


Figure 21. X-ray diffraction pattern of gibbsite
(a) no O.M. added - 2 weeks
(b) no O.M. added - 3 months
(c) O.M.I added (C:Al ratio 1.52) - 4 weeks
(d) O.M.I added (C:Al ratio 1.52) - 3 months

aging. Broadening of the peak indicated that O.M.I interfered with the formation and growth of gibbsite crystals. High concentrations of O.M.I completely inhibited the formation of crystalline aluminum hydroxide. Anions such as Cl^-, SO_4^{--} were considered to cause distortion of $Al(OH)_3$ lattice and prevent growth of large crystals (Barnhisel and Rich 1963).

X-ray diffraction data of the Al hydroxy-clays and the hydroxy-clay-O.M.I complexes, aged for 3 months showed the presence of gibbsite in all cases (Table 14). The peak at 4.85 Å (gibbsite) of the O.M.I treated hydroxy Al clay was diffuse and broad compared with the sharp peak in the control hydroxy-clay (Figure 22). It was possible to detect a small 4.85 Å peak (gibbsite) in the OH/Al = 2.7 ratio clay, 1 month after preparation. The OH/Al = 2.5 ratio clay or the O.M.I treated clays (both 2.5 and 2.7 ratios) did not give any gibbsite peak at the end of 1 month. Electron micrographs (Figure 13a, 14a, section IV.2.3), showed the presence of not too well crystallized $Al(OH)_3$ in the 2.5 and 2.7 ratio hydroxy-clays at 1 month's time. The inhibition of formation of gibbsite at 1 month time may not be entirely a pH effect (Table 4, section IV.2.1), since both the acid and neutralised O.M.I showed the same effect. After 3 Months' aging, the <u>d</u> spacing of the control clays as well as that of O.M. treated ones,

TABLE 14. X-ray diffraction data of Al hydroxy-clay-O.M.I complexes aged 3 months

	Air dry Å	6 hrs. at 100°C Å	24 hrs. at 200°C Å	Gibbsite Å
1. $\frac{OH}{Al}$ = 2.5-clay	17.8	14.6	14.6	4.85-sharp
2. $\frac{OH}{Al}$ = 2.5-clay-O.M.I (pH2.86)	17.2	14.2	14.2	4.85-broad
3. $\frac{OH}{Al}$ = 2.5-clay-O.M.I (pH 7.0)	17.4	14.8	14.4	4.85-broad
4. $\frac{OH}{Al}$ = 2.7-clay	17.2	14.2	14.6	4.85-sharp
5. $\frac{OH}{Al}$ = 2.7-clay-O.M.I (pH2.86)	17.2	14.8	14.6	4.85-broad
6. $\frac{OH}{Al}$ = 2.7-clay-O.M.I (pH 7.0)	17.4	15.1	14.8	4.85-broad

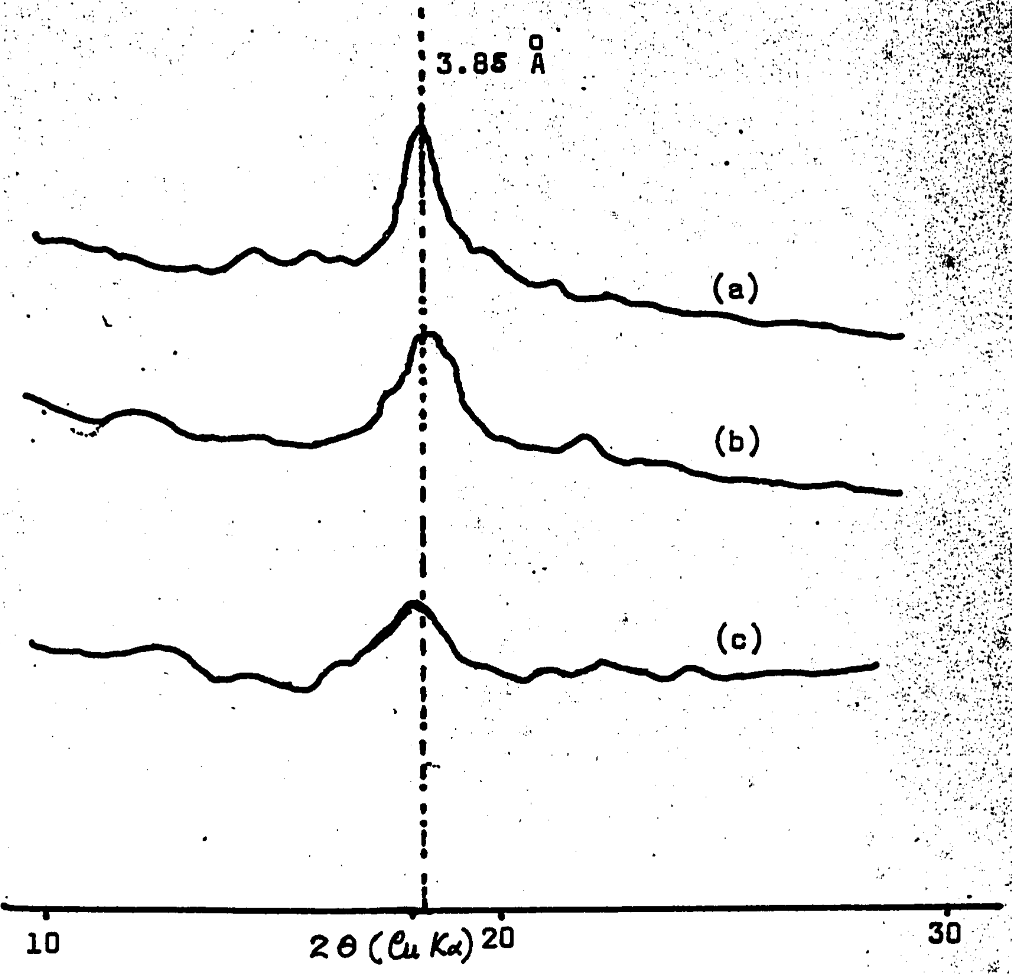
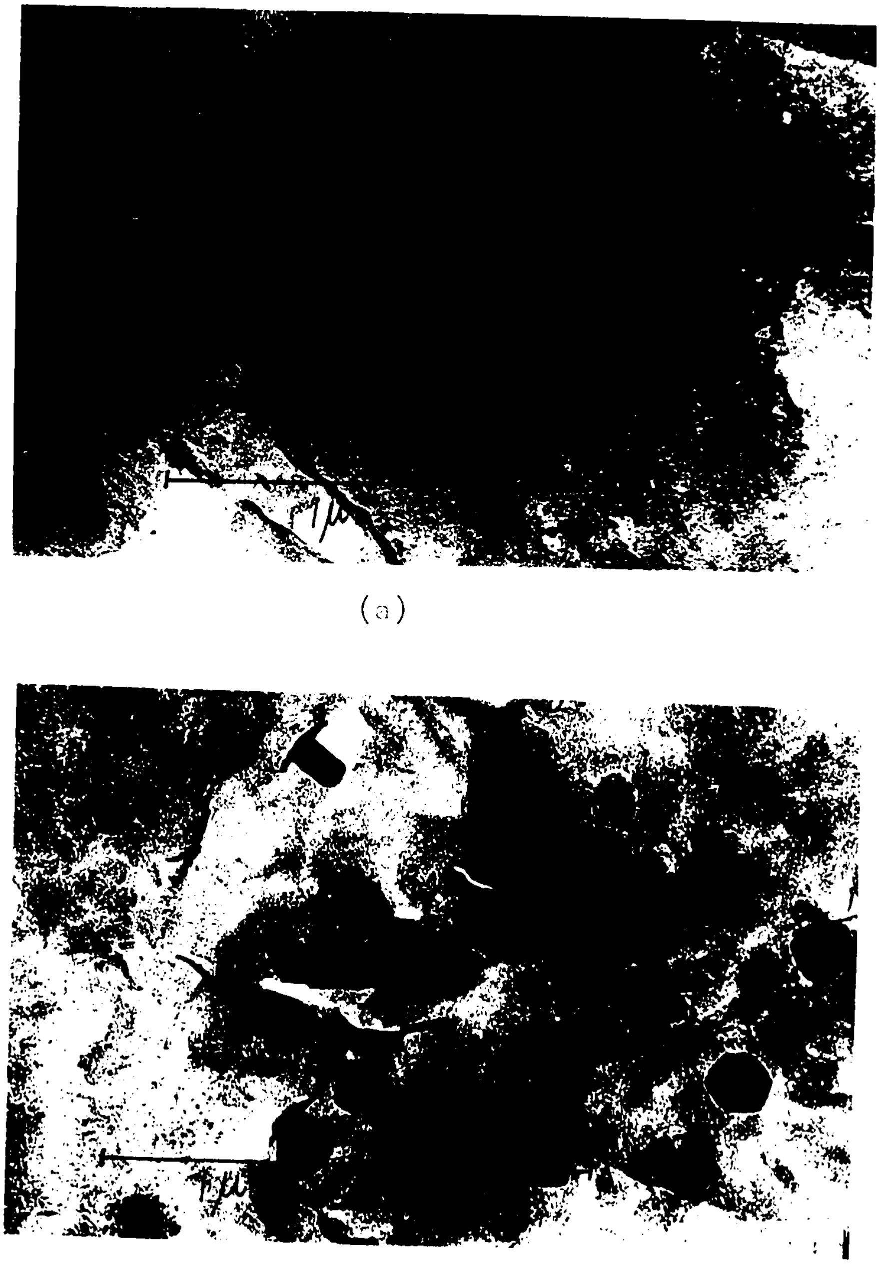


Figure 22. X-ray diffraction pattern of gibbsite formed from Al hydroxy-montmorillonite aged 3 months
(a) OH/Al-2.7 clay
(b) OH/Al-2.7 clay-O.M.I(pH 7.0)
(c) OH/Al-2.7 clay-O.M.I(pH 2.8)

decreased from 16.6 Å to 14.6 Å (200°C values, Tables 7 and 14), indicating the formation of gibbsite from interlayer hydroxide (Barnhisel and Rich 1963). The presence of O.M.I on the external surface did not seem to affect the formation of gibbsite from interlayer hydroxide.

Electron micrographs of the 3 months aged hydroxy-clay-O.M.I complexes showed clearly the presence of gibbsite crystals only in the case of 2.7 ratio clay-O.M. complexes (Figure 23a, b). The size and amount of gibbsite crystals was smaller in the acid O.M.I treated clay (gibbsite crystals shown by arrows in Figure 23a) than in the neutral O.M.I treated clay (Figure 23b). This may have been due to the lower pH and higher amount of O.M.I adsorbed in the former than in the latter case (Table 4, section IV.2.1). In the case of OH/Al = 2.5 ratio clay-O.M.I complexes, a few particles which appeared to be larger than the O.M.I particles, were seen (shown by arrows in Figure 23c,d), but it was not possible to tell definitely whether these were gibbsite crystals. However, X-ray diffraction gave a broad peak at 4.85 Å. It is possible that the presence of an appreciable amount of O.M.I in these preparations would have prevented growth of larger crystals.

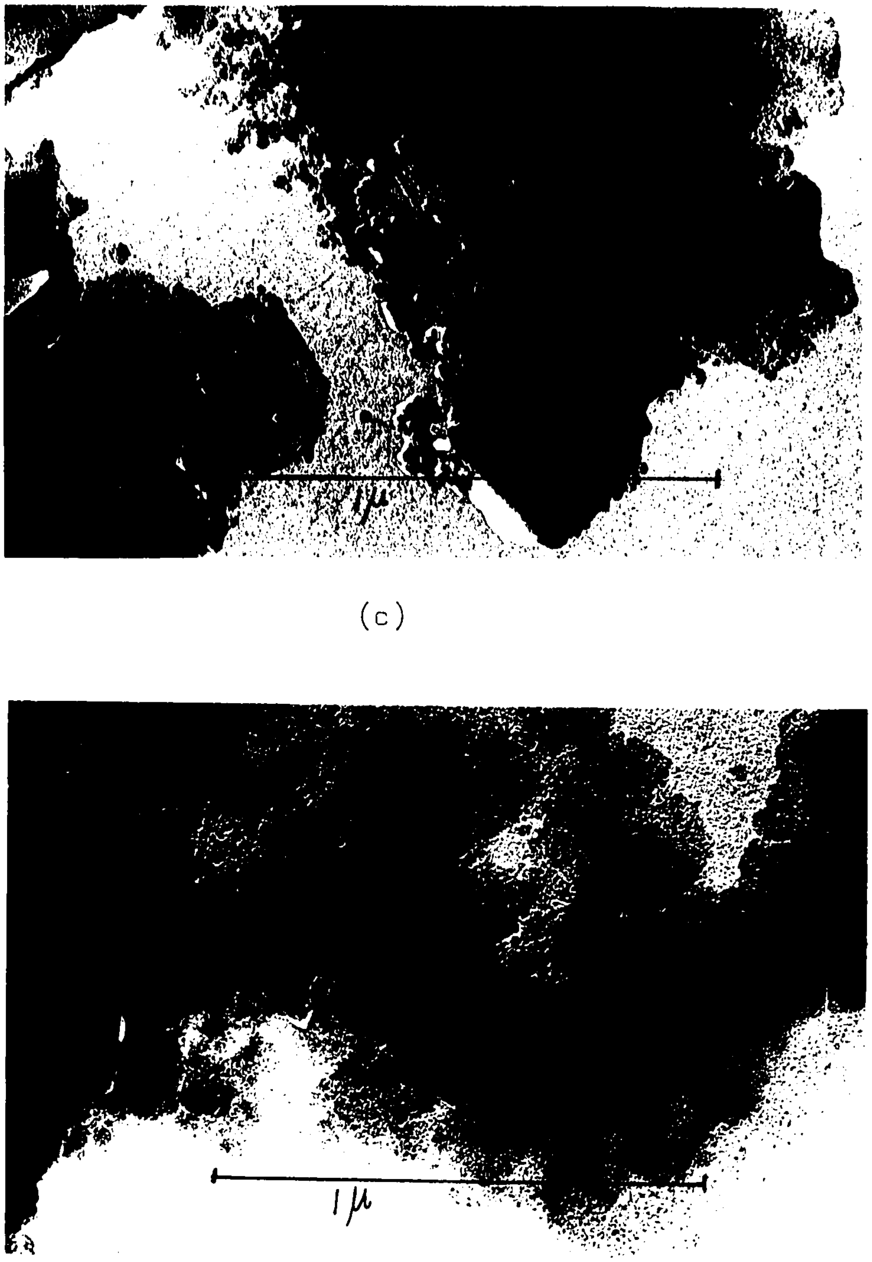
The results discussed above showed that O.M. had an inhibitory or retarding effect on the formation of gibbsite. Presence of O.M. on the external surface of the clay did not



(a)

(b)

Figure 23. Electron micrographs of Al hydroxy-clay-O.M.I complexes aged 3 months.
(a) OH/Al = 2.7 clay-O.M.I(pH 2.8).
(b) OH/Al = 2.7 clay-O.M.I(pH 7.0).



(c)

(d)

Figure 23. Electron micrographs of Al hydroxy-clay-O.M.I complexes aged 3 months.
(c) OH/Al = 2.5 clay-O.M.I(pH 2.8)
(d) OH/Al = 2.5 clay-O.M.I(pH 7.0)

prevent the formation of gibbsite from interlayer positions. These observations are consistent with the results of other experiments reported in this dissertation, and support the proposed mechanism of carboxyl groups displacing OH groups in Al hydroxy compounds.

V. SUMMARY AND CONCLUSIONS

Studies on adsorption of soil organic matter by bentonite clay coated with either Al or Fe hydroxy compounds are reported in this thesis.

The adsorption of O.M. preparations used in this study was higher at lower pH values than at pH 7. However, noticeable adsorption took place even at pH 7 on the Al, Fe hydroxy-clays. Hydroxy Fe-clays adsorbed more O.M. than the hydroxy Al-clays. Adsorption by hydroxy Al or Fe clay was higher than Na-clay or Al^{3+} or Fe^{3+} saturated clay. The adsorption data conformed approximately to the Langmuir isotherm, but deviations were also observed at both low and high concentrations of O.M.

Desorption of adsorbed O.M. showed that respectively 18-25% and 20-30% of the O.M. adsorbed by hydroxy Al and hydroxy Fe-clays could not be desorbed by 0.5 N Na_2CO_3, but was completely desorbed by 0.5 N Na OH. In the case of Al^{3+} or Fe^{3+} saturated clays, too, 15-20% of the adsorbed O.M. behaved similarly. O.M. adsorbed by Na-clay was almost completely desorbed by 0.5 N Na_2CO_3.

X-ray diffraction data indicated that the O.M. used in this study was not adsorbed in the interlamellar space of the clay. Electron micrographs of the hydroxy clay-O.M. complexes showed the association of O.M. with both the edge and planar faces of the hydroxy-clays.

Electrostatic interaction, hydrogen bonding and coordination of carboxyls of O.M. to Al or Fe in the hydrous oxide coatings on clay surface were suggested as possible mechanisms of bonding of O.M. to hydroxy Al or Fe clays. The O.M. not desorbed by 0.5 N Na_2CO_3 was considered to be held by multiple bonding, possibly chelation with Al or Fe of the hydroxy compounds, augmented by hydrogen bonding and Van der Waals forces. It was suggested that hydrogen bonds formed with the hydroxyl of the Al, Fe hydroxy compounds through the oxygen of the carboxyl group or carboxylate ion would be stable at higher pH values. It was not possible to determine the exact contribution of each mechanism, since all three, electrostatic interaction, hydrogen bonding and coordination were all pH dependent and tended to behave similarly with increases in pH. High adsorption may have been favoured by the higher charge on the polynuclear hydroxy ions on surfaces, low zeta potential, expanded lattice and the higher possibility of hydrogen bonding in the systems studied.

pH values of mixtures of model organic compounds, O.M., and Al, Fe hydroxy solutions or Al, Fe hydroxy clays were found to increase shortly after mixing. The increase was explained as due to "anion penetration," where the carboxylate groups displaced OH groups coordinated to Al or Fe in the respective hydroxy compounds. "Anion penetration" reaction was observed to be slower in the hydroxy Fe systems than in the hydroxy Al systems. Infra-red spectra of complexes of O.M. with hydroxy Al, Fe compounds were interpreted as indicating the formation of both simple ionic and coordinate bonds, the coordinate bonds being predominantly ionic in character. Determination of OH/Al ratio of hydroxy Al solutions at different pH values in the presence and absence of O.M. showed that the OH/Al ratio was lower in the presence of O.M. up to pH 7.6. This was interpreted to mean that O.M. could successfully compete with OH ions for coordination sites around Al at lower pH values. Data of OH/Al ratios at higher pH values (>7.6) were inconclusive. Based on these results, it was concluded that O.M. displaced OH groups coordinated to Al or Fe in the respective hydroxides at low pH values and a reversal of the reaction took place at higher pH values or higher OH ion concentration. Such a reaction could account for part of the O.M. bonded to Al, Fe hydroxy-clays.

O.M. used in this study was observed to exert an inhibitory or retarding effect on the formation of X-ray crystalline $Al(OH)_3$ from amorphous Al hydrous oxide. No gibbsite (or any other crystalline $Al(OH)_3$) was formed from hydroxy Al solutions at pH 8, in the presence of O.M. when the C:Al ratio was greater than or equal to 2.51. Even at C:Al ratio of 1.52, the X-ray diffraction peak of the product obtained was diffuse and broad, which indicated that the O.M. interfered with the formation and growth of the crystal lattice. In the case of the hydroxy Al-clays, formation of gibbsite was retarded but after 3 months' aging it was possible to detect gibbsite. It was not possible to determine whether this gibbsite was formed from interlayer hydrous oxide only or from hydrous oxide on external surface of the clay also. Presence of O.M. on the external surface did not seem to affect the formation of gibbsite from interlayer hydrous oxide.

LITERATURE CITED

Ahlrichs, J. L. 1962.
Bonding of organic polyanions to clay minerals.
Diss. Abs. 22: 2121.

Aldrich, D. G., and Buchanan, J. R. 1958.
Anomalies in techniques for preparing H-bentonite.
Soil Sci. Soc. Amer. Proc. 22: 281-285.

Aleksandrova, L. N. 1954.
The nature and products of reaction of humic acid and humates with sesquioxides.
Soils and Ferts. 17: Abs. 962.

________. 1967.
Organo-mineral humic acid derivatives and methods of studying them.
Soviet Soil Sci. No. 7: 903-913.

Aleksandrova, L. N., and M. Nad. 1958.
The nature of organo-mineral colloids and methods of their study.
Soviet Soil Sci. No. 10: 1100-1105.

Aveston, J. 1965.
Hydrolysis of the Aluminum ion: Ultra-centrifugation and acidity measurements.
J. Chem. Soc. 4438-4443.

Bailar, J. C., Jr. 1956.
Chemistry of the Coordination Compounds.
Reinhold Pub. Co., N.Y.

Bailey, G. W., J. L. White, and T. Rothberg. 1968.
Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate.
Soil Sci. Soc. Amer. Proc. 32: 222-234.

Barnhisel, R. I. 1969.
Changes in specific surface areas of clays treated with hydroxy-aluminum.
Soil Sci. 107: 126-130.

Barnhisel, R. I., and C. I. Rich. 1963.
Gibbsite formation from aluminum interlayers in montmorillonite.
Soil Sci. Soc. Amer. Proc. 27: 632-635.

Bellamy, L. J. 1958.
The Infra-red Spectra of Complex Molecules
John Wiley and Sons Inc., N.Y.

Beutelspacher, H. 1955.
Interaction between the inorganic and organic colloids in soil.
Z. Pflernähr. Düng. 69: 108-115, cited by Greenland, D. J., 1965b, in Interaction between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties.
Soils and Ferts. 28: 521-532.

Beutelspacher, H., and H. W. Van der Marel. 1968.
Atlas of electron microscopy of clay minerals and their admixtures.
Elsevier Pub. Co. N.Y.

Bingham, F. T., J. R. Sims, and A. L. Page. 1965.
Retention of acetate by montmorillonite.
Soil Sci. Soc. Amer. Proc. 29: 670-672.

Bloomfield, C. 1957.
The possible significance of polyphenols in soil formation.
J. Sci. Fd. Agric. 8: 389-392.

Bradley, W. F. 1945.
Molecular associations between montmorillonite and some poly-functional organic liquids.
J. Amer. Chem. Soc. 67: 975-981.

Bremner, J. M. 1965.
Total Nitrogen. In Agronomy 9, C. A. Black, ed. Methods of Soil Analysis.
American Society of Agronomy, Madison, Wis., pp. 1149-1178.

Bremner, J. M., Heintze, S. G., P. J. G. Mann, and H. Lees. 1946.
Metallo-organic complexes in soil.
Nature 158: 790-791.

Brindley, G. W. 1951.
X-ray identification and crystal structures of clay minerals.
The Mineralogical Society, London.

Brindley, G. W., and R. W. Hoffmann. 1962.
Orientation and packing of aliphatic chain molecules on montmorillonite.
Clays and clay minerals 9: 546-556.
Pergamon Press, N.Y.

Broadbent, F. E. 1953.
The soil organic fraction
Advanc. Agron. 5: 153-183.

Broadbent, F. E., and G. R. Bradford. 1952.
Cation exchange groups in the soil organic fraction.
Soil Sci. 74: 447-457.

Brooks, J. D., and S. Sternhell. 1957.
Chemistry of brown coals. I. Oxygen containing functional groups in Victorian brown coals.
Austr. J. Appl. Sci. 8: 206-221.

Brossett, C. 1952.
On the reactions of the aluminum ion with water.
Acta Chem. Scand. 6: 910-940.

Brossett, C., G. Biedermann, and L. G. Sillén. 1954.
Studies on hydrolysis of metal ions. XI. The aluminum ion Al^{3+}.
Acta Chem. Scand. 8: 1917-1926.

Brown, G. 1953.
The dioctahedral analogue of vermiculite.
Clay Min. Bull. 2: 64-69.

Brydon, J. E., and H. Kodama. 1966.
The nature of aluminum hydroxide-montmorillonite complexes.
Am. Mineral. 51: 875-879.

Brydon, J. E., and F. J. Sowden. 1959.
A study of the clay-humus complex of a chernozemic and podzolic soil.
Can. J. Soil Sci. 39: 136-143.

Busch, D. H., and J. C. Bailar. 1953.
The stereochemistry of complex inorganic compounds. XVII. The stereochemistry of hexadentate ethylene diamine tetra acetic acid complexes.
J. Amer. Chem. Soc. 75: 4574-4575.

Carolan, R. 1948.
Modification of Graham's method for determining soil organic matter by colorimetric analysis.
Soil Sci. 66: 241-247.

Chaberek, S., and A. E. Martell. 1959.
Organic Sequestering Agents.
John Wiley and Sons, N.Y.

Chang, M. L., and G. W. Thomas. 1963.
A suggested mechanism for sulphate adsorption by soils.
Soil Sci. Soc. Amer. Proc. 27: 281-283.

Cifrulak, S. D. 1967.
Spectroscopic evidence of phthalates in soil organic matter.
Soil Sci. 107: 63-69.

Clark, J. S. 1964.
Some cation exchange properties of soils containing free oxides.
Can. J. Soil Sci. 44: 203-211.

Clark, J. S., and W. E. Nichol. 1968.
Reactions of iron hydrous oxide with Wyoming bentonite.
Can. J. Soil Sci. 48: 173-183.

Coleman, N. T., and G. W. Thomas. 1967.
Chemistry of Soil Acidity <u>In</u> Agronomy 12, R. W. Pearson and F. Adams, ed. Soil Acidity and Liming.
American Society of Agronomy, Madison, Wis., pp. 1-41

Coleman, N. T., G. W. Thomas, F. H. LeRoux, and G. Bredell. 1964.
Salt-exchangeable and titratable acidity in bentonite-sesquioxide mixtures.
Soil Sci. Soc. Amer. Proc. 28: 35-37.

Coulson, C. B., R. I. Davies, and D. A. Lewis. 1960.
Polyphenols in plant, humus and soil. II. Reduction and transport by polyphenols of iron in model soil columns.
J. Soil Sci. 11: 20-44.

Davey, B. G., and P. F. Low. 1968.
Clay-water interactions as affected by hydrous aluminum oxide films.
Int. Congr. Soil Sci. Trans. 9th (Adelaide) I: 607-616.

Day, P. R. 1965.
Particle fractionation and particle-size analysis.
In Agronomy 9, C. A. Black, ed. Methods of Soil Analysis.
American Society of Agronomy, Madison, Wis., pp. 545-567.

De Haan, F. A. M., and G. H. Bolt. 1963.
Determination of anion adsorption by clays.
Soil Sci. Soc. Amer. Proc. 27: 636-640.

Demolon, A., and G. Barbier. 1929.
C. R. Acad. Sci. 188: 654, cited by Evans, L. T., and E. W. Russell in The adsorption of humic and fulvic acids by clays.
J. Soil Sci. 10: 119-132.

De Villiers, J. M., and M. L. Jackson. 1967.
Aluminous chlorite origin of pH dependent cation exchange capacity variations.
Soil Sci. Soc. Amer. Proc. 31: 614-619.

Diamond, S., and E. B. Kinter. 1956.
Surface areas of clay minerals as derived from measurements of glycerol retention.
Clays and clay minerals 5: 334-347.
Pergamon Press, N.Y.

Dixon, J. B., and M. L. Jackson. 1962.
Properties of intergradient chlorite-expansible layer silicates of soils.
Soil Sci. Soc. Amer. Proc. 26: 358-362.

Dosch, W. 1967.
Interlamellar reactions of tetracalcium aluminate hydrate with water and organic compounds.
Clays and Clay minerals 27: 273-292.
Pergamon Press, N.Y.

Dubach, P., and N. C. Mehta. 1963.
The chemistry of soil humic substances.
Soils and Ferts. 26: 293-300.

Dubach, P., G. Zweifel, R. Bach, *et al*. 1955.
Examination of the fulvic fraction of some Swiss soils.
Z. PflEnähr. Düng. 69: 97-108, cited by Greenland, D. J., 1965b *in* Interaction between clays and organic compounds in soisl. Part II. Adsorption of soil organic compounds and its effect on soil properties.
Soils and Ferts. 28: 521-532.

D'Yakonova, K. V. 1962.
Iron humus complexes and their role in plant nutrition.
Soviet Soil Sci. No. 7: 692-698.

Edsall, J. T., and J. Wymann. 1958.
Biophysical chemistry, Vol. I.
Academic Press Inc. N.Y.

Edwards, D. G., A. M. Posner, and J. P. Quirk. 1965.
Repulsion of chloride ions by negatively charged clay surfaces. Part III. Di and Trivalent ions.
Trans. Faraday Soc. 61: 2820-2823.

Emerson, W. W. 1955.
Complex formation between montmorillonite and high polymers.
Nature 176: 461.

________. 1956a.
A comparison between the mode of action of organic matter and synthetic polymers in stabilising soil crumbs.
J. Agric. Sci. 47: 350-353.

________. 1956b.
Synthetic soil conditioners.
J. Agric. Sci. 47: 117-121.

Emerson, W. W. 1960.
Complexes of calcium-montmorillonite with polymers
Nature 186: 573-574.

________. 1963.
The effect of polymers on the swelling of montmorillonite.
J. Soil Sci. 14: 52-63.

Evans, L. T., and E. W. Russell. 1959.
The adsorption of humic and fulvic acids by clays.
J. Soil Sci. 10: 119-132.

Falk, M., and D. G. Smith. 1963.
Structure of carboxyl groups in humic acids.
Nature 200: 569.

Felbeck, Jr., G. T. 1965.
Structural chemistry of soil humic substances.
Advanc. Agron. 17: 328-368.

Flaig, W., and H. Beutelspacher. 1951.
Electron microscope investigations on natural and synthetic humic acids.
Z. Pfl. Ernähr. Düng. 52: 1-21, cited by Greenland, D. J. 1965b <u>in</u> Interaction between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties.
Soils and Ferts. 28: 521-532.

________. 1955.
Physical chemistry of humic acids (In German).
Land bounkund, Tijdschr. B.66, N 5-6, Cited by Aleksandrova, L. N. and M. Nad, 1958, <u>in</u> The nature of organo-mineral colloids and methods of their study.
Soviet Soil Sci. No. 10: 1100-1105.

Flaschka, H. A., and A. J. Barnard, Jr. 1967.
Chelates in Analytical Chemistry.
Marcel Dekker Inc. N.Y.

French, R. O., M. E. Wadsworth, M. A. Cook, and I. B. Cutler. 1954.
The quantitative application of infra red spectroscopy to studies in surface chemistry.
J. Phys. Chem. 58: 805-811.

Frink, C. R. 1965.
Characterisation of aluminum interlayers in soil clays.
Soil Sci. Soc. Amer. Proc. 29: 379-382.

Frink, C. R., and M. Peech. 1963a.
Hydrolysis and exchange reactions of the aluminum ion in hectorite and montmorillonite suspensions.
Soil Sci. Soc. Amer. Proc. 27: 527-530.

________. 1963b.
Hydrolysis of aluminum ion in dilute aqueous solutions.
Inorg. Chem. 2: 473-478.

Frink, C. R., and B. L. Sawhney. 1967.
Neutralisation of dilute aqueous aluminum salt solutions.
Soil Sci. 103: 144-147.

Fripiat, J. J., F. Van Cauwelaert, and H. Bosmans. 1965.
Structure of Al cations in aqueous solutions.
J. Phys. Chem. 69: 2458-2461.

Fuoss, R. M., and G. I. Cathers. 1949.
Polyelectrolytes.
J. Polymer Sci. 4: 97-120.

Fuoss, R. M., and U. M. Strauss. 1948.
Electrostatic interaction of polyelectrolytes and simple electrolytes.
J. Polymer Sci. 3: 602-603.

Gastuche, M. C., and M. M. Mortland. 1964.
Crystallisation of mixed iron and aluminum gels.
Soil Sci. 98: 281-289.

Gillam, W. S. 1940.
A study on the chemical nature of humic acid.
Soil Sci. 49: 433-453.

Gimblett, F. G. R. 1963.
Inorganic Polymer Chemistry.
Butterworth and Co. Ltd. London.

Greenland, D. J. 1956.
The adsorption of sugars by montmorillonite.
II. Chemical studies.
J. Soil Sci. 7: 329-334.

Greenland, D. J. 1963.
Adsorption of polyvinyl alcohols by montmorillonite.
J. Colloid Sci. 18: 647-664.

________. 1965a.
Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and defined organic compounds.
Soils and Ferts. 28: 415-425.

________. 1965b.
Interaction between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties.
Soils and Ferts. 28: 521-532.

Greenland, D. J., and G. W. Ford. 1964.
Separation of partially humified organic materials from soils by ultrasonic dispersion.
Int. Congr. Soil Sci. Trans. 8th (Bucharest) III: 137-148.

Grim, R. E. 1953.
Clay Mineralogy.
McGraw-Hill Book Co. Inc., N.Y.

Hartford, W. H. 1942.
Chromic acid anodic baths: Interpretation of glass electrode measurements.
In. Eng. Chem. 34: 920-924.

Hemwall, J. B. 1963.
Adsorption of 4-tert-butyl pyrocatechol by soil clay minerals.
Int. Clay Cont. Proc. (Stockholm) 1: 319-328.
The Macmillan Co. N.Y.

Herera, R., and M. Peech. 1968.
Reactions of montmorillonite with iron (III).
Agron. Abs. p. 81. American Society of Agronomy, Madison, Wis.

Hingston, F. J., R. Atkinson, A. M. Posner, and J. P. Quirk. 1968.
Specific adsorption of anions on goethite.
Int. Cong. Soil Sci. Trans. 9th (Adelaide) I: 669-678.

Hoffmann, R. W., and G. W. Brindley. 1960.
Adsorption of non ionic aliphatic molecules from aqueous solutions on montmorillonite. Clay organic studies II.
Geochim. Cosmochim. Acta 20: 15-29, cited by Greenland, D. J. 1965a, in Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and defined organic compounds.
Soils and Ferts. 28: 415-425.

Holmes, R. M., and S. J. Toth. 1957.
Physico-chemical behaviour of clay-conditioner complexes.
Soil Sci. 84: 479-487.

Hsu, P. H. 1966.
Formation of gibbsite from ageing hydroxy-aluminum solutions.
Soil Sci. Soc. Amer. Proc. 30: 173-176.

Hsu, P. H., and T. F. Bates. 1964a.
Formation of X-ray amorphous and crystalline hydroxides.
Min. Mag. 33: 749-768.

________. 1964b.
Fixation of hydroxy-aluminum polymers by vermiculite.
Soil Sci. Soc. Amer. Proc. 28: 763-769.

Jacks, G. V. 1963.
Biological nature of soil productivity.
Soils and Ferts. 26: 147-150.

Jackson, M. L. 1960.
Soil Chemical Analysis.
Prentice-Hall Inc. N.J.

________. 1963.
Aluminum bonding in soils: A unifying principle in soil science.
Soil Sci. Soc. Amer. Proc. 27: 1-10.

Jander, G., and A. Winkel. 1931.
Z. Anorg. Chem. 20: 257, cited by Ruff, J. K. and S. Y. Tyree, 1958, in Light scattering studies on aluminum nitrate solutions.
J. Amer. Chem. Soc. 80: 1523-1526.

Jones, L. H., and D. A. Thurman. 1957.
The determination of aluminum in soil, ash, and plant materials using Eriochrome-Cyanine R.
Plant and Soil. 9: 131-142.

Jung, J. E. 1943.
Bodenk. Pfl. Ernähr. 32: 325, cited by Evans, L. T. and E. W. Russell, 1959, in The Adsorption of humic and fulvic acids by clays.
J. Soil Sci. 10: 119-132.

Jurinak, J. J. 1966.
Surface chemistry of hematite: Anion penetration effect on water adsorption.
Soil Sci. Soc. Amer. Proc. 30: 559-562.

Kawaguchi, K., and K. Kyuma. 1959.
On the complex formation between soil humus and polyvalent cations. Soil and Plant Food 5: 54, cited by Kononova, M. M. 1966, in Soil Organic Matter.
Pergamon Press, N.Y.

Kawaguchi, K., and K. Kyuma. 1961.
On the complex formation between soil humus and polyvalent cations.
Soils and Ferts. 24: Abs. 62.

Khan, D. V. 1946.
The fixation of humic acid by various minerals.
Dokl. Vsesoywz. Akad. S-kh. Nauk. Lenina. 1-2, cited by Kononova, M. M., 1966, in Soil Organic Matter.
Pergamon Press, N.Y.

________. 1950.
The adsorption of organic matter by soil minerals.
Soils and Ferts. 14: Abs. 535.

Khanna, S. S., and F. J. Stevenson. 1962.
Metallo-organic complexes in soil. I. Potentiometric titration of some soil organic matter isolates in the presence of transition metals.
Soil Sci. 93: 298-305.

Kittrick, J. A. 1965.
Electron microscope techniques. In Agronomy 9, C. A. Black, ed., Methods of Soil Analysis.
American Society of Agronomy, Madison, Wis. pp. 632-652.

Kirschner, S., and R. Kiesling. 1960.
The structure of copper (II) tartrate trihydrate.
J. Amer. Chem. Soc. 82: 4174-4176.

Kobo, K., and T. Fujisawa. 1964.
Studies on the clay-humus complex. 3. Adsorption of humic acid by clay.
Soils and Ferts. 27: Abs. 1274.

Kohl, R. A., and S. A. Taylor. 1961.
Hydrogen bonding between carbonyl group and Wyoming bentonite.
Soil Sci. 91: 223-227.

Kononova, M. M. 1966.
Soil Organic Matter.
Pergamon Press, N.Y.

Kononova, M. M., I. V. Aleksandrova, and N. A. Titova. 1964.
Decomposition of silicates by organic substances in the soil.
Soviet Soil Sci. No. 10: 1005-1014.

Kroth, E. M., and J. B. Page. 1946.
Aggregate formation in soils with special reference to cementing substances.
Soil Sci. Soc. Amer. Proc. 11: 27-34.

Kubelka, 1949.
J. Am. Leather. Chem. Assoc. 44: 824, cited by Bailar, J. C., 1956, in Chemistry of the Coordination Compounds.
Reinhold Pub. Co., N.Y.

Laby, R. H. 1962.
Adsorption of amino acids and peptides by montmorillonite. Ph.D. thesis, Univ. of Adelaide, cited by Greenland D. J., 1965a, in Interaction between clays and organic compounds in soils. Part I. Mechanisms of interaction between clays and defined organic compounds.
Soils and Ferts. 28: 415-425.

Lamb, A. B., and A. G. Jacques. 1938.
The slow hydrolysis of ferric chloride in dilute solution. II. Change in hydrogen ion concentration.
J. Amer. Chem. Soc. 60: 1215-1255.

Leaver, J. P., and E. W. Russell. 1957.
The reaction between phosphate and phosphate fixing soils.
J. Soil Sci. 8: 113-126.

Levashkevich, G. A. 1966.
Interaction of humic acids with iron and aluminum hydroxides.
Soviet Soil Sci. No. 4: 422-427.

Levesque, M., and M. Schnitzer. 1965.
Effects of NaOH concentration on the extraction of organic matter and of major inorganic constituents from a soil.
Can. J. Soil Sci. 46: 7-12.

Lindner, R. C., and C. P. Harley. 1942.
A rapid method for the determination of nitrogen in plant material.
Science 96: 565-566.

Ling Ong, H., and R. E. Bisque. 1968.
Coagulation of humic colloids by metal ions.
Soil Sci. 106: 220-224.

Liu, M., and G. W. Thomas. 1961.
Nature of sulphate retention by acid soils.
Nature 192: 384.

MacEwan, D. M. C. 1948.
Complexes of clays with organic compounds.
Trans. Faraday Soc. 44: 349-367.

Marion, S. P., and A. W. Thomas. 1946.
Effect of diverse anions on the pH of maximum precipitation of "Aluminumhydroxide."
J. Colloid Sci. 1: 221-234.

Martell, A. E., and M. Calvin. 1952.
Chemistry of the metal chelate compounds.
Prentice-Hall Inc., N.Y.

Martin, A. E. 1960.
Chemical studies of Podzolic illuvial horizons.
V. Flocculation of humus by ferric and ferrous iron and by nickel.
J. Soil Sci. 11: 382-392.

Martin, A. E., and R. Reeve. 1958.
Chemical studies of Podzolic illuvial horizons.
III. Titration curves of organic-matter suspension.
J. Soil Sci. 9: 89-100.

_______. 1960.
Chemical studies of Podzolic illuvial horizons.
IV. The flocculation of humus by aluminum.
J. Soil Sci. 11: 369-381.

Matijevic, E., Mathoi, R., Ottewill, R. H., and M. Kerker. 1961.
Detection of metal ion hydrolysis by coagulation.III.
J. Phys. Chem. 65: 826-830.

Matijevic, E., and B. Tezak. 1953.
Coagulation effects of aluminum nitrate and aluminum sulphate on aqueous solutions of silver halides.
J. Phys. Chem. 57: 951-954.

Mattson, S. 1931.
The laws of soil colloidal behaviour. VI. Amphoteric behaviour.
Soil Sci. 32: 343-365.

Mattson, S., and L. Wicklander. 1940.
The pH and amphoteric behaviour of soils in relation to the Donnan equilibrium.
Ann. Agr. Coll. Swed. 8: 1-54, cited by Coleman, N. T., and G. W. Thomas, 1967, in Chemistry of Soil Acidity. Agronomy 12, Pearson, R. W., and F. Adams, ed., Soil Acidity and Liming.
American Society of Agronomy, Madison, Wis., pp. 1-41.

McKeague, J. A. 1968.
Humic-fulvic acid ratio, Al, Fe and C in pyrophosphate extracts as criteria of A and B horizons.
Can. J. Soil Sci. 48: 27-35.

McLean, E. O. 1965.
Aluminum. In Agronomy 9, C. A. Black, ed., Methods of Soil Analysis.
American Society of Agronomy, Madison, Wis., pp. 978-998.

Milburn, R. M., and W. C. Vosburgh. 1955.
A spectrophotometric study of the hydrolysis of Fe III ion. II. Polynuclear species.
J. Amer. Chem. Soc. 77: 1352-1355.

Mitchell, B. D., V. C. Farmer, and W. J. McHardy. 1964.
Amorphous inorganic materials in soils.
Advanc. Agron. 16: 327-383.

Morris, M. L., and D. H. Busch. 1956.
The properties and I.R. absorption spectra of complexes of cobalt (III) with pentadentate E.D.T.A. and hexa ethylene-triamine triacetic acid.
J. Amer. Chem. Soc. 78: 5178-5181.

Mortensen, J. L. 1957.
Adsorption of hydrolysed poly-acrylonitrile on kaolinite. I. Effect of exchange cations and anions.
Soil Sci. Soc. Amer. Proc. 21: 385-388.

————. 1959.
Adsorption of hydrolysed poly-acrylonitrile on kaolinite. II. Effect of solution electrolytes.
Soil Sci. Soc. Amer. Proc. 23: 199-202.

————. 1962.
Adsorption of hydrolysed poly-acrylonitrile on kaolinite.
Clays and Clay minerals, 11: 530-545.
Pergamon Press, N.Y.

————. 1963.
Complexing of metals by soil organic matter.
Soil Sci. Soc. Amer. Proc. 27: 179-186.

————. 1965.
Partial extraction of organic matter. In Agronomy 9, C. A. Black, ed. Methods of Soil Analysis.
American Society of Agronomy, Madison, Wis., pp. 1401-1408.

Mortland, M. M. 1966.
Urea complexes with montmorillonite: An infrared absorption study.
Clay minerals 6: 143-156.

Mukherjee, P. N., and A. Lahiri. 1956.
Rheological properties of humic acid from Coal.
J. Colloid Sci. 11: 240-243.

Myers, H. E. 1937.
Physico-chemical reactions between organic and inorganic soil colloids as related to aggregate formation.
Soil Sci. 44: 331-357.

Nakamoto, K. 1963.
Infra-red spectra of Inorganic and Coordination Compounds.
John Wiley and Sons, N.Y.

Olsen, S. R., and F. S. Watanabe. 1957.
A method to determine a phosphorous adsorption maximum of soils as measured by the Langmuir isotherm.
Soil Sci. Soc. Amer. Proc. 21: 144-149.

Olson, R. V. 1965.
Iron. <u>In</u> Agronomy 9, C. A. Black ed., Methods of Soil Analysis.
American Society of Agronomy, Madison, Wis. pp. 963-973.

Packter, A. 1957.
Interaction of montmorillonite clays with polyelectrolytes.
Soil Sci. 83: 335-343.

Parfitt, R. L., and M. M. Mortland. 1968.
Ketone adsorption on montmorillonite.
Soil Sci. Soc. Amer. Proc. 32: 355-363.

Pauling, L. 1960.
Nature of the Chemical Bond.
Cornell Univ. Press, Ithaca, N.Y.

Paulson, R. V., and J. F. Murphy. 1956.
Simple indicator method for determination of aluminum.
Anal. Chem. 28: 1182-1184.

Piret, E. L., <u>et al</u>. 1960.
Some physico-chemical properties of peat humic acids.
Sci. Proc. Royal Dublin Soc., Series A, 1: 69-80, cited by LingOng, H., and R. E. Bisque, 1968, <u>in</u> Coagulation of humic colloids by metal ions.
Soil Sci. 106: 220-224.

Pokras, L. 1956.
On the species present in aqueous solutions of salts of polyvalent metals.
J. Chem. Ed. 33: 152-161.

Posner, A. M. 1966.
The humic acids extracted by various reagents from a soil.
J. Soil Sci. 17: 65-78.

Rappoport, Z. 1967.
Hand book of tables for organic compound identification (3rd ed.).
The Chemical Rubber Co., Cleveland, Ohio.

Raupach, M. 1963.
Solubility of simple aluminum compounds expected in soils. I. Hydroxides and oxy-hydroxides.
Austr. J. Soil Res. 1: 28-35.

Rausch, W. V., and H. D. Bale. 1964.
Small angle X-ray scattering from hydrolysed Al-nitrate solutions.
J. Chem. Phys. 40: 3391-3394.

Rich, C. I. 1960.
Aluminum in interlayers of vermiculite.
Soil Sci. Soc. Amer. Proc. 24: 26-32.

________. 1968.
Hydroxy interlayers in expansible layer silicates.
Clays and Clay Minerals 16: 15-30.
Pergamon Press, N.Y.

Rich, C. I., and S. S. Obenshain. 1955.
Chemical and clay mineral properties of a Red-Yellow Podzolic soil derived from muscovite schist.
Soil Sci. Soc. Amer. Proc. 19: 334-341.

Rich, C. I., and G. W. Thomas. 1960.
The clay fraction of soils.
Advanc. Agron. 12: 1-39.

Ruehrwein, R. A., and S. Ward. 1952.
Mechanisms of clay aggregation by polyelectrolytes.
Soil Sci. 73: 485-492.

Ruff, J. K., and S. Y. Tyree. 1958.
Light scattering studies on aqueous aluminum nitrate solutions.
J. Amer. Chem. Soc. 80: 1523-1526.

Russell, E. W. 1961.
Soil Conditions and Plant Growth, 9th ed.
Longmans, Green and Co., Ltd., London.

________. 1963.
The role of organic matter in soil productivity.
In The use of isotopes in soil organic matter studies, Report of the F.A.O./I.A.E.A., technical meeting, Volkenrode, 1963.
Pergamon Press, N.Y.

Saini, G. R., and A. A. MacLean. 1966.
Adsorption-flocculation reactions of soil polysaccharides with kaolinite.
Soil Sci. Soc. Amer. Proc. 30: 697-699.

Sawhney, B. L. 1968.
Aluminum interlayers in layer silicates: Effect of OH/Al ratio of Al solution, time of reaction and type of structure.
Clays and Clay Minerals, 16: 157-163.
Pergamon Press, N.Y.

Sawyer, D. T., and J. M. McKinnie. 1960.
Properties and infra red spectra of E.D.T.A. complexes. III. Chelates of higher valent ions.
J. Amer. Chem. Soc. 82: 4191-4196.

Sawyer, D. T., and P. J. Paulsen. 1958.
Properties and infra red spectra of E.D.T.A. complexes. I. Alkaline earth chelates.
J. Amer. Chem. Soc. 80: 1957-1600.

Scheffer, F., and B. Ulrich. 1960.
Humus und Humus-Düngung.
Ferdinand Enke Verlag Stuttgart, cited by Wright, J. R., and M. Schnitzer, 1963, in Metallo-organic interactions associated with podzolisation.
Soil Sci. Soc. Amer. Proc. 27: 171-176.

Schnitzer, M. 1965.
The application of infra-red spectroscopy to investigations on soil humic compounds.
Can. Spectroscopy 10: 121-127.

Schnitzer, M., and U. C. Gupta. 1964.
Some chemical characteristics of the organic matter extracted from the O and B_2 horizons of a Gray Wooded soil.
Soil Sci. Soc. Amer. Proc. 28: 374-377.

Schnitzer, M., and H. Kodama. 1967.
Reactions between a Podzol fulvic acid Na-montmorillonite.
Soil Sci. Soc. Amer. Proc. 31: 632-636.

Schnitzer, M., D. A. Shearer, and J. R. Wright. 1959.
A study in the infra red of high molecular weight organic matter extracted by various reagents from a Podzolic B horizon.
Soil Sci. 87: 252-257.

Schnitzer, M., and S. I. Skinner. 1963a.
Organo-metallic interactions in soils. 1. Reactions between a number of metal ions and the organic matter of a Podzol Bh horizon.
Soil Sci. 96: 86-93.

________. 1963b.
Organo-metallic interactions in soils. 2 Reactions between different forms of iron and aluminum and the organic matter of a Podzol Bh horizon.
Soil Sci. 96: 181-186.

________. 1964.
Organo-metallic interactions in soils. 3 Properties of iron and aluminum organic matter complexes prepared in the laboratory and extracted from a soil.
Soil Sci. 98: 197-203.

________. 1965.
Organo-metallic interactions in soils. 4 Carboxyl and hydroxyl groups in organic matter and metal retention.
Soil Sci. 99: 278-284.

Schofield, R. K. 1940.
Clay mineral structures and their physical significance.
Trans. Ceram. Soc. (Engl.) 39: 147-158, cited by Grim, R. E. 1953, in Clay Mineralogy.
McGraw-Hill Book Co., Inc., N.Y.

________. 1946.
Factors influencing ion exchange in soils.
Soils and Ferts. 9: 265-267.

Schofield, R. K. 1949.
Calculation of surface area of clays from measurements of negative adsorption.
Trans. Ceram. Soc. (Engl.) 48: 207-213, cited by Grim, R. E., 1953, <u>in</u> Clay Mineralogy.
McGraw-Hill Book Co., Inc., N.Y.

Schofield, R. K., and A. W. Taylor. 1954.
Hydrolysis of aluminum salt solutions.
J. Chem. Soc. 4445-4448.

Schulz, W. 1958.
Some observations on short term changes in soils on a small scale.
Z. Pfl. Ernähr Düng. 80: 66-70, cited by Greenland, D. J. 1965b, <u>in</u> Interaction between clays and organic compounds. Part II. Adsorption of soil organic compounds and its effect on soil properties.
Soils and Ferts. 28: 521-532.

Schwertmann, U. 1966.
Inhibitory effect of soil organic matter on the crystallisation of goethite.
Nature 212: 645-646.

Schwertmann, U., W. R. Fischer, and H. Papendorf. 1968.
The influence of organic compounds on the formation of iron oxides.
Int. Congr. Soil Sci. Trans. 9th (Adelaide) I: 645-655.

Sedletsky, I. D., and L. Tatarinova. 1941.
Electronographic studies of soil colloids.
Pochvovedenie No. 9: 33-43, cited by Greenland, D. J. 1965b, <u>in</u> Interaction between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties.
Soils and Ferts. 28: 521-532.

Sen, B. C. 1960.
Studies on the adsorption of humic acid on H-clays and role of metal cations in humus adsorption.
J. Ind. Chem. Soc. 37: 793-797.

Shapiro, R. E., and M. Fried. 1959.
Relative release and retentiveness of soil phosphates.
Soil Sci. Soc. Amer. Proc. 23: 195-198.

Shen, M. J., and C. I. Rich. 1962.
Aluminum fixation in montmorillonite.
Soil Sci. Soc. Amer. Proc. 26: 33-36.

Sheppard, N. 1959.
Infra red spectra of adsorbed molecules.
Spectrochimica Acta. 14: 249-260.

Sheraga, H. A. 1961.
Protein Structure.
Academic Press, Inc. N.Y.

Siddall, T. H., and W. C. Vosburgh. 1951.
A spectrophotometric study of the hydrolysis of iron (III) ion.
J. Amer. Chem. Soc. 73: 4270-4272.

Sillén, L. G. 1959.
Quantitative studies of hydrolytic equilibria.
Quart. Revs. 13: 146-168.

Simha, R., H. L. Frisch, and F. R. Eirich. 1953.
The adsorption of flexible macromolecules.
J. Phys. Chem. 57: 584-589.

Slaughter, M., and I. H. Milne. 1960.
The formation of chlorite like structures from montmorillonite.
Clays and Clay Minerals 5: 114-124.
Pergamon Press, N.Y.

Steel, R. G. D., and J. H. Torrie. 1960.
Principles and Procedures of Statistics.
McGraw-Hill Book Co. Inc., N.Y.

Stevenson, F. J. 1965.
Gross chemical fractionation of organic matter.
<u>In</u> Agronomy 9, C. A. Black, ed., Methods of Soil Analysis.
American Society of Agronomy, Madison, Wis., pp. 1409-1421.

Swaby, R. J. 1950.
The influence of humus on soil aggregation.
J. Soil Sci. 1: 182-194.

Swenson, R. M., C. V. Cole, and D. H. Sieling. 1949.
Fixation of phosphate by iron and aluminum and replacement by organic and inorganic ions.
Soil Sci. 67: 3-22.

Tahoun, S. A., and M. M. Mortland. 1966.
Complexes of montmorillonite with primary, secondary and tertiary amides. II. Coordination of amides on the surface of montmorillonite.
Soil Sci. 102: 314-321.

Tensmeyer, L. G., R. W. Hoffmann, and G. W. Brindley. 1960.
Infra-red studies of some complexes between ketones and calcium montmorillonite.
J. Phys. Chem. 64: 1655-1662.

Theng, B. K. G., and A. M. Posner. 1967.
Nature of the carbonyl groups in humic acid.
Soil Sci. 104: 191-201.

Theng, B. K. G., J. R. H. Wake, and A. M. Posner. 1966.
The infra-red spectrum of humic acid.
Soil Sci. 102: 70-72.

Thomas, A. W., and C. B. Kremer. 1935.
Hydrous thoria sols considered as polynuclear basic thorium complexes.
J. Amer. Chem. Soc. 57: 1821-1824.

Thomas, A. W., and R. D. Vartanian. 1935.
The action of acids on hydrous alumina.
J. Amer. Chem. Soc. 57: 4-7.

Thomas, A. W., and T. H. Whitehead. 1931.
Ion interchange in aluminum oxychloride hydrosols.
J. Phys. Chem. 35: 27-47.

Thomas, G. W., and A. R. Swoboda. 1963.
Cation exchange in kaolinite-iron oxide systems.
Clays and Clay Minerals.11: 321-326.

Turner, R. C. 1965.
Some properties of aluminum hydroxide precipitated in the presence of clays.
Can. J. Soil Sci. 45: 331-336.

Turner, R. C. 1967.
Aluminum removed from solutions by montmorillonite.
Can. J. Soil Sci. 47: 217-222.

Turner, R. C. 1968.
Conditions in solution during the formation of gibbsite in dilute Al salt solutions. I. Theoretical treatment of the effect of the formation of mono- and polynuclear hydroxy Al ions, precipitations and crystallisation on curves representing titration of $AlCl_3$ with a base.
Soil Sci. 106: 291-296.

Turner, R. C., and J. E. Brydon. 1965.
Factors affecting the solubility of $Al(OH)_3$ precipitated in the presence of montmorillonite.
Soil Sci. 100: 176-181.

Van Olphen, H. 1963.
An Introduction to Clay Colloid Chemistry.
Interscience Publishers, N.Y.

Visser, S. A. 1963.
Electron microscope and electron diffraction pattern of humic acids.
Soil Sci. 45: 353-357.

Wagner, G. H., and F. J. Stevenson. 1965.
Structural arrangement of functional groups in soil humic acid as revealed by infra red analysis.
Soil Sci. Soc. Amer. Proc. 29: 43-48.

Warkentin, B. P. 1956.
Bonding between montmorillonite clay particles.
Diss. Abs. 16: 1354.

Warkentin, B. P., and R. D. Miller. 1958.
Conditions affecting formation of the montmorillonite polyacrylic acid bond.
Soil Sci. 85: 14-18.

Watts, H. L. 1958.
Volumetric determination of aluminum in the presence of iron, titanium, calcium, silicon, and other impurities.

Weast, R. C. 1968.
Hand book of Chemistry and Physics, 48th ed.
The Chemical Rubber Co., Cleveland, Ohio.

Welcher, F. J. 1958.
The analytical uses of E.D.T.A.
Van Nostrand Publ. Co., N.Y.

Whittig, L. D. 1965.
X-ray diffraction techniques for mineral identification and mineralogical composition. In Agronomy 9, C. A. Black (ed.), Methods of Soil Analysis. American Society of Agronomy, Madison, Wis. pp. 671-698.

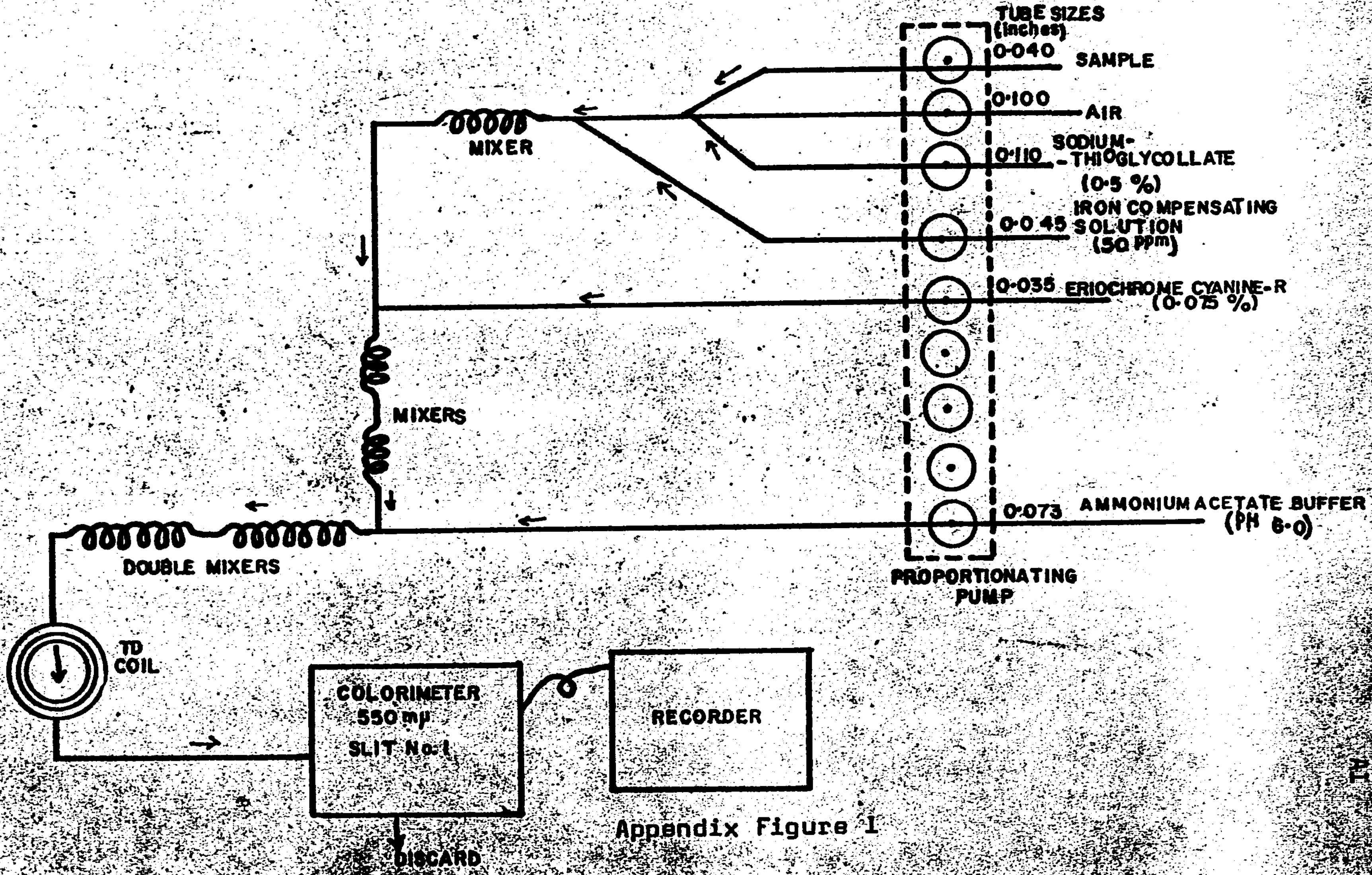
Wood, J. C., S. E. Moschopedis, and W. Den Hertog. 1961
Studies in humic acid chemistry. II. Humic anhydrides. Fuel 40: 491-502, cited by Wagner, G.H. and F. J. Stevenson, 1965, in Structural arrangement of functional groups in soil humic acids as revealed by infra red analysis.
Soil Sci. Soc. Amer. Proc. 29: 43-48

Wright, J. R., and M. Schnitzer. 1959.
Oxygen-containing functional groups in the organic matter of a Podzol.
Nature 184: 1462-1463.

________. 1961.
An estimate of the aromaticity of the organic matter of a Podzol soil.
Nature 190: 703-704.

Yuan, T. L. 1959.
Determination of exchangeable hydrogen in soils by a titration method.
Soil Sci. 88: 164-167.

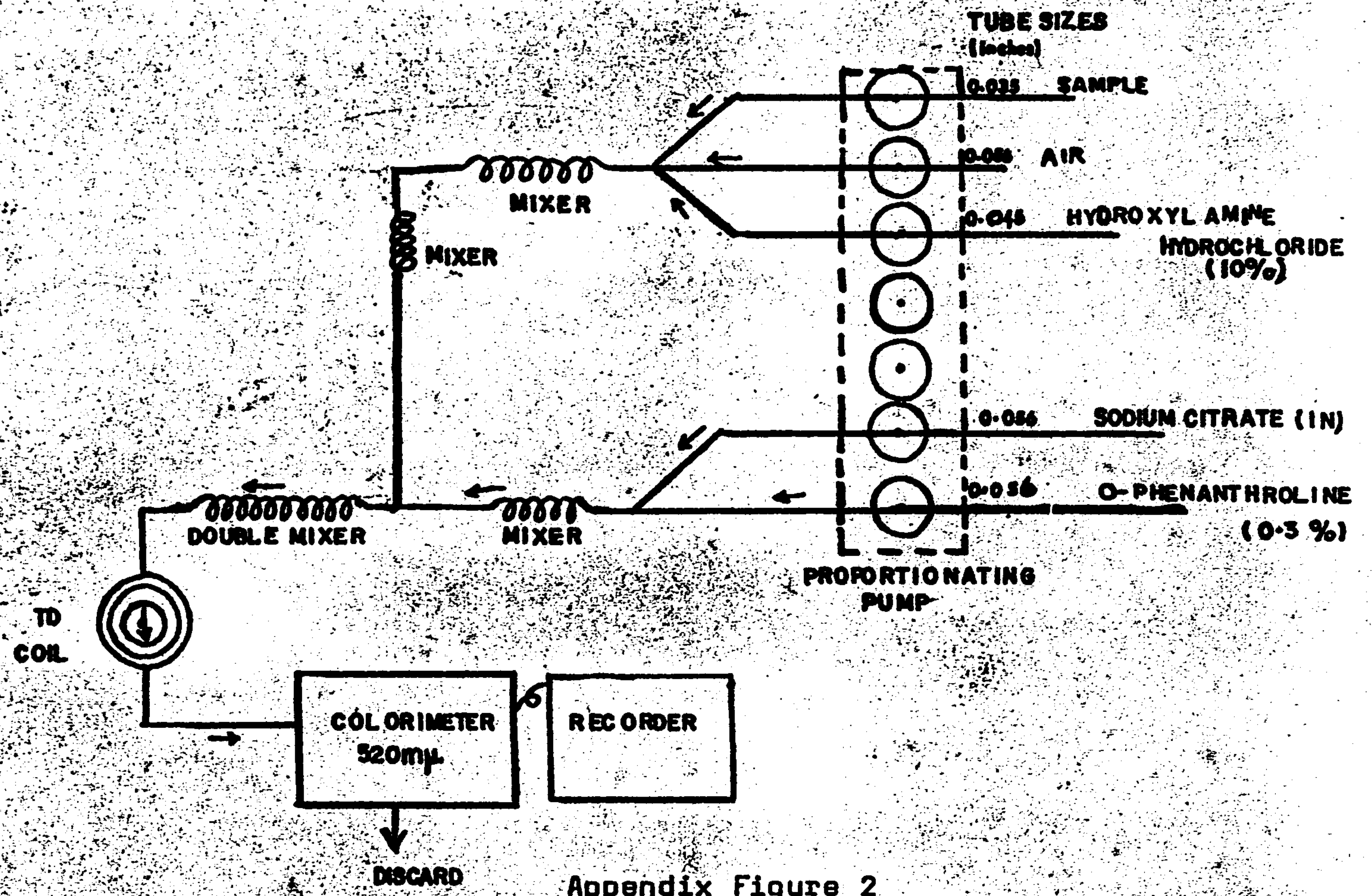
FLOW DIAGRAM FOR ALUMINUM DETERMINATION



Appendix Figure 1

AI

FLOW DIAGRAM FOR IRON DETERMINATION



Appendix Figure 2

APPENDIX TABLE 1. Adsorption of O.M.I on OH/Al = 2.5-clay (pH 4.5)

Equilibrium concentration (c) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	2.39	0.00418
0.021	3.67	0.00572
0.101	8.23	0.0123
0.141	12.6	0.0112
0.262	15.1	0.0173
0.578	13.5	0.0428
0.737	20.4	0.0361

APPENDIX TABLE 2. Adsorption of O.M.II on OH/Al = 2.5-clay (pH 4.5)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	2.50	0.0040
0.101	3.68	0.0274
0.121	9.1	0.0133
0.141	14.6	0.00968
0.354	15.8	0.0224
0.818	16.7	0.0491
0.980	19.8	0.0493

APPENDIX TABLE 3. Adsorption of O.M.I on OH/Al = 2.5-clay (pH 7.0)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	1.24	0.00806
0.040	2.48	0.0161
0.101	4.67	0.0216
0.141	7.16	0.0197
0.303	7.87	0.0385
0.478	8.47	0.0564

APPENDIX TABLE 4. Adsorption of O.M.I on OH/Al = 2.7-clay (pH 5.2)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	2.39	0.00418
0.030	4.56	0.00658
0.080	8.68	0.00922
0.091	13.6	0.00665
0.273	14.9	0.0183
0.576	13.9	0.0413
0.697	21.3	0.0327

APPENDIX TABLE 5. Adsorption of O.M.II on OH/Al = 2.7-clay (pH 5.2)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	2.98	0.00336
0.061	5.00	0.0122
0.101	10.4	0.00964
0.141	15.9	0.00883
0.333	17.8	0.0187
0.747	14.4	0.0518
0.989	21.3	0.0464

APPENDIX TABLE 6. Adsorption of O.M.I on OH/Al = 2.7-clay (pH 7.0)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	1.52	0.00658
0.040	2.72	0.0147
0.101	5.12	0.0197
0.121	8.17	0.0148
0.192	10.4	0.0184
0.424	10.0	0.0420

APPENDIX TABLE 7. Adsorption of O.M.I on OH/Fe = 2.5-clay (pH 3.3)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	3.48	0.00287
0.020	6.37	0.00314
0.061	12.2	0.00502
0.111	17.6	0.00629
0.465	14.3	0.0326
0.515	19.8	0.0260
0.707	28.1	0.0252

APPENDIX TABLE 8. Adsorption of O.M.II on OH/Fe = 2.5-clay (pH 3.3)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	3.66	0.00273
0.020	7.31	0.00274
0.061	14.0	0.00434
0.081	21.3	0.00379
0.192	26.0	0.00738
0.515	24.5	0.0210
0.727	33.2	0.0219

APPENDIX TABLE 9. Adsorption of O.M.I on OH/Fe = 2.5-clay (pH 7.0)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.020	2.50	0.00797
0.091	3.54	0.0257
0.273	4.43	0.0616
0.343	8.56	0.0401
0.495	10.3	0.0479
0.616	10.1	0.0610
1.110	11.2	0.0980

APPENDIX TABLE 10. Adsorption of O.M.I on OH/Fe = 2.7-clay (pH 3.5)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	3.74	0.00267
0.020	7.50	0.00267
0.040	15.0	0.00267
0.101	21.1	0.00479
0.323	21.7	0.0149
0.545	22.2	0.0245
0.758	31.3	0.0242

APPENDIX TABLE 11. Adsorption of O.M.II on OH/Fe = 2.7-clay (pH 3.5)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	4.31	0.00232
0.030	8.26	0.00363
0.101	15.1	0.00667
0.121	23.8	0.00509
0.212	29.9	0.00707
0.485	29.8	0.0163

APPENDIX TABLE 12. Adsorption of O.M.I on OH/Fe = 2.7-clay (pH 7.0)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	3.29	0.00304
0.051	5.55	0.00919
0.232	6.59	0.0352
0.293	11.8	0.0248
0.495	12.2	0.0407
0.667	13.5	0.0493

APPENDIX TABLE 13. Adsorption of O.M.I on Al^{3+}-clay (pH 3.8)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.020	2.11	0.00948
0.051	4.05	0.0126
0.081	8.4	0.0096
0.182	11.4	0.0159
0.414	11.5	0.0360
0.444	15.9	0.0278

APPENDIX TABLE 14. Adsorption of O.M.I on Fe^{3+}-clay (pH 3.0)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.010	2.50	0.0040
0.040	4.55	0.00879
0.071	9.35	0.00759
0.172	12.5	0.0138
0.394	12.9	0.0306
0.444	15.0	0.0296
0.828	18.3	0.0452

APPENDIX TABLE 15. Adsorption of O.M.I on H-Na clay (pH 4.5)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.091	0.48	0.189
0.152	1.49	0.102
0.333	2.43	0.137
0.444	4.67	0.0951
0.636	5.47	0.116
0.859	5.74	0.150
1.374	5.08	0.270

APPENDIX TABLE 16. Adsorption of O.M.I on Na-clay (pH 7.0)

Equilibrium concentration (C) mg O.M./ml	Amount adsorbed (x/m) g O.M./100g clay	$\frac{C}{(x/m)}$
0.091	0.174	0.523
0.192	0.348	0.552
0.384	0.690	0.557
0.556	0.870	0.639
0.808	0.690	1.17
1.273	-	-
1.434	0.870	1.65