PHYSICO-CHEMICAL STUDIES OF SOME TRANSFORMED MONTMORILLONITE CLAYS

Thesis submitted for the award of
the Degree of
DOCTOR OF PHILOSOPHY
in Chemistry

By
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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE
September, 1966

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CERTIFICATE

Certified that the thesis entitled " Physico-chemical studies of some transformed montmorillonite clays", which is being submitted,by Mr.Gian Chand Gupta, for the award of the degree of Doctor of Philosophy, in Chemistry, of the University of Roorkee, is a record of his own work,carried out under my guidance and supervision. The matter embodied in this thesis has not been submitted for the award of any other degree of any University.

This is,further, to certify that he has worked, for a period of two years and over eight months,from December 26,1963 to September 16,1966,at this University to prepare this thesis.

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Gupta.

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List of techniques used in these investigations.

1. X-Ray Diffractometry.
2. Infra Red Spectrophotometry.
3. Differential Thermal Analysis.
4. Dehydration Studies.
5. Stain Tests.
6. Cation Exchange Capacity Measurements.
7. Flame Photometric Analysis.
8. Chemical Analysis.
9. Polarographic Reduction Behaviour.
10. Potentiometric Titrations.
11. Conductivity Measurements.
12. Viscometric Behaviour.
13. Suspension Effect and Sol Concentration Effect Studies.

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2. Chapter I.

3. Chapter II.

4. Chapter III.

5. Chapter IV.

GENERAL INTRODUCTION

Soil and its constitution:

oxygen

Silicon and aluminum are the most abundant of the elements constituting the earth. Clay-the powder obtained from the disintegration of rocks, is, chemically, ferro-alumino-silicate, of varying composition, with some other elements like sodium, potassium, calcium, magnesium etc. thrown in. Physically it consists of particles of diameters ranging from 1.0 mm to 0.00001 mm in varying proportions.

The definition of soil(1)as a mass of inorganic material that holds inorganic and organic colloids, dead and living plant and animal material, water and gases in variable but balanced proportions has lost much of its original significance. Soil is much more complex than what this definition conveys. Broadly speaking, it consists of four components, namely, mineral materials, organic matter, water and air. The most important and yet highly intriguing constituent, to which the soil complexity may be attributed, is its mineral matter, consisting of particles of varying size; those in the finer state of subdivision($<$0.002 mm) form the clay fraction of the soil and the coarse ones consist of mainly rock debris(2).

Clay minerals study and its importance:

Clay minerals have been studied for a great many years, but within the last thirty years, great strides have been made not only by soil chemists, but by investigators from very many different disciplines. This has been possible mainly due to increasing importance of clay mineralogy in industry and technology(3), substantiated with the results in the field of mineralogy and emergence of new instrumental techniques.

In the ceramic industry,only some particular clays can be used to manufacture these ceramic products. Studies of the changes taking place when clay minerals are heated to elevated temperatures have greatly enhanced our knowledge in this field,(4,5).

In the oil industry,certain types of bentonite clays are essential,for the preparation of the muds,required for the drilling of oil wells,while a different type of bentonite, forms the basis of many of the catalysts,used in the refining of petroleum products,(6,7).

Certain types of kaolinites are used as fillers and coating materials in the paper industry. Research into structure and properties of kaolinite has resulted in improvements of such paper properties as acceptance to ink, rate of drying etc.,(8,9).

On the basis of the empirical laboratory data the engineer has tried to ascertain conditions for soil stabilization,(10).

Similarly for the geologist and the agricultural research workers,the treatment of the subject depends to a very large extent on the proper knowledge,of the clay mineral composition,of the soil and rock debris,(2,11,12).

Origin of clay minerals:

All the various clay minerals,with the possible exception of attapulgite-palygorskite and vermiculite,have been authentically reported in hydrothermal bodies. In many hydrothermal clay bodies a zonal arrangement of clay minerals has been observed. Often there is an inner halo of sericite (white mica alteration product), an intermediate zone of kaolinite, and an outer zone of montmorillonite and chlorite; chlorite being most abundant on the outermost fringe, (2).

On the basis of their classic study at Montana, Sales and Myer(13) concluded that alteration is essentially contemporaneous with ore deposition. Lovering (14) and Kerr (15) have described wall rock alteration, at numerous deposits, which seems to have developed in stages.

Chloritic mica and vermiculite were reported as minor constituents, in a clay mineral analysis, of series of sediments from Eastern France and Germany by Millot(16). The illitic and chloritic clay minerals found in slates have a higher crystallinity and are composed of layer units more regularly oriented. Grim et al(17) identified chloritic clay mineral, in some samples from the Gulf of California, and the Pacific Ocean off the California coast, and also concluded from their data that kaolinite is very slowly being lost in these marine sediments, probably by alteration to illite or chloritic mica. It seems certain that chloritic mica and illite also tend to form during marine diagenesis from other minerals.

<u>Laboratory synthesis of clay minerals</u>:

a. Synthesis from mixtures of oxides and hydroxides at elevated temperatures and pressures:- Noll(18) working with silica and alumina gels, between 250° - 500°C, claimed the formation of kaolinite with some other different phases. On the other hand, Roy(19) has shown that halloysite may be the resulting phase in the system Al_2O_3-SiO_2-H_2O rather than kaolinite.

b. Synthesis from mixtures of crystalline minerals and chemical reagents at elevated temperatures and pressures:- According to Gruner(20) kaolinite,pyrophillite,muscovite and boehmite are the phases formed,when microline and albite are subjected to high temperatures and pressures,in presence of $Al(OH)_3$,SiO_2 and KCl under acid conditions.Badger and Ally (21) produced kaolinite,on heating potash feldspar for 24 hrs., at 225°C under a pressure of 1800 p.s.i., in presence of 5% hydrofluoric acid.

c. Synthesis from mixtures of oxides and hydroxides at ordinary temperature and pressure:-Sedletsky(22)mixed sodium silicate and sodium aluminate,leached it with 1 N $MgCl_2$, washed the product and after four years of ageing,identified a product similar to montmorillonite. Caillere and Henin (23) reported the synthesis of clay minerals,by electrolysis of solution of silica,or alumina-silica mixture. The product depended on the nature of the anode used. Aluminum anode gives kaolinite while with a magnesium anode antigorite is formed.

d. Transformations of clay minerals at ordinary temperature and pressure:- Many investigators including Caillere and Henin (24),Volk(25),Aleshin(26) and Barshad(27) have shown that a material substantially like illite is produced, from montmorillonite when all its exchange positions are occupied by potassium ions, and the material is dried at 110°C. Formation of kaolinite from montmorillonite,by its treatment with 20% $CaCl_2$, 0.5% Na_3AlO_3 and 10% $Al(NO_3)_3$ for 3-4 days and then with HCl or NH_4OH has been reported by Caillere and Henin(28). The latter authors(29) have further shown that the treatment of montmorillonite, under certain conditions, with a solution containing Mg^{++} ions so that all the exchange positions are occupied by the magnesium ions, produces a product having the characteristics of chlorite.

Synthesis of chlorite:

Most of the work cited in the literature on chlorites has been done by Caillere and Henin. The widespread occurrence of different varieties of chlorites, in soils and sedimentary rocks, has been explained frequently as the result of precipitation of hydroxides of magnesium, iron, or aluminum between the unit sheets of expanding clay minerals. This explanation has been supported by reports of the laboratory preparation of chlorite like materials as a result of the precipitation of hydroxides in montmorillonite suspensions. The original description of this process was given by Caillere and Henin (loc.cit.). Subsequent papers by Caillere and Henin(30), Longuet Escard(31) and Youell (32) have indicated, that the hydroxides or hydrous oxides, of magnesium, aluminum, nickel, cobalt, zinc and ferrous iron, can form montmorillonite-hydroxide complexes.

A wide variation exists under which these chlorite like structures have been prepared. Caillere and Henin (loc.cit.) used fairly concentrated suspension-solution mixtures, containing 6% clay and 1 N to 4 N concentration of $MgCl_2$. The precipitation of magnesium hydroxide was carried out by dropwise addition of ammonium hydroxide solution accompanied by vigorous shaking. Longuet Escard (loc.cit.), on the other hand, reported the formation of aluminum hydroxide and nickel hydroxide complexes with montmorillonite, in systems containing 0.5 - 1.0 % clay and less than 0.1 N concentration of metal nitrates. Youell (loc.cit), reported, without details, a successful electrolytic method of precipitating magnesium and zinc hydroxides within the interlayer space of montmorillonite.

Slaughter and Milne(33) have prepared chlorite-like complexes of montmorillonite with magnesium hydroxide and other hydroxides, under a variety of physical and chemical conditions. Requirements for the preparation of these complexes have been simplified considerably by the use of rapid mixing techniques. A complex may be formed either by precipitating the hydroxide in a clay suspension, or by preparing the precipitate separately and mixing it with the clay suspension immediately. These studies had been undertaken to assess the possible geological significance of this method of formation of chlorite.

Structure of clay minerals:

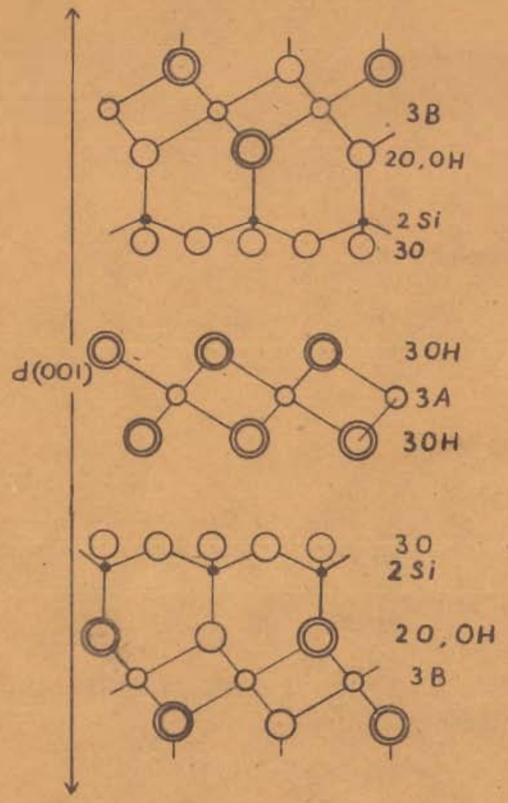
The older concepts that the clay minerals are particles more or less spherical, have now been replaced by newer one, Shaw(34). It is now well established that the particles are laminated, i.e., made up of layers of plates or flakes, the individual size and shape depending upon their mineralogical organisation and the conditions in which they have developed e.g.hexagonal blades,rods or fluffy.

For long,clays were considered to be composed of amorphous matter and all attempts to interpret their properties had to be based on the findings of strictly chemical methods of investigation. Extensive studies of X-Ray diffraction patterns have revealed that even the finest fraction of clays are crystalline in nature and composed of comparatively few and simple building units,(35,36). The difference in the properties of various clays is now believed to depend on the spatial arrangement of these units in the crystal lattice.

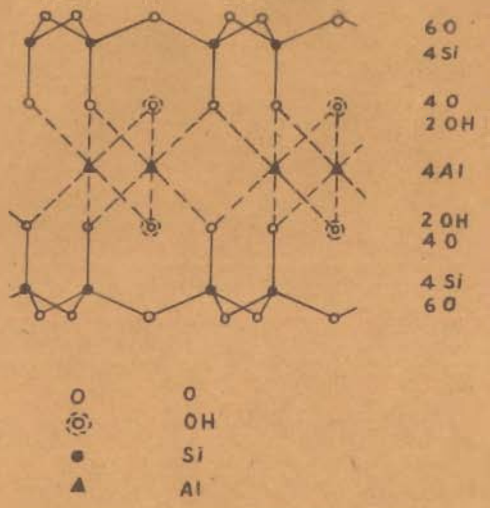
The structure of the common clay minerals have been determined in considerable details,by numerous investigators, based on the generalisations of Pauling(37). Two structural units are involved in the atomic lattice of most of the clay minerals. The first consists of a silicon tetrahedron,in which a silicon atom is equidistant from four oxygens or hydroxyls,the silicon being in the centre. The second unit consists of two sheets of closely packed oxygens or hydroxyls in octahedral co-ordination,so that they are equidistant from six oxygens or six hydroxyls. Combination of these structural units(held by chemical forces),with modifications, finally gives rise to the structure of clay minerals,that are found in the colloid clay fractions of soils.

a. Structure of kaolinite:- It is a hydrous aluminum silicate of approximate composition Al_2O_3 $2SiO_2$ $2H_2O$. Its structure was first suggested by Pauling(loc.cit.) and worked out in details by Gruner(38) and Brindley et al (39). In kaolinite, a single silica tetrahedral sheet is topped with a slightly distorted gibbsite sheet,both being formed by condensation and splitting off of water between adjoining hydroxyl group in vertex position. All the tips of the silica tetrahedrons point in the same direction and towards the centre of the unit made of silica and alumina sheets. The mineral can thus be described as,having a 1:1,non expanding lattice.Structural formula may be expressed as $(OH)_8 Al_4Si_4O_{10}$ and the size of the unit cell is 7.2 A. The space lattice is such that there is little substitution of ions in its structure and there are no unsatisfied valencies on the cleavage surface. Cation exchange capacity (c.e.c.) is insignificant.

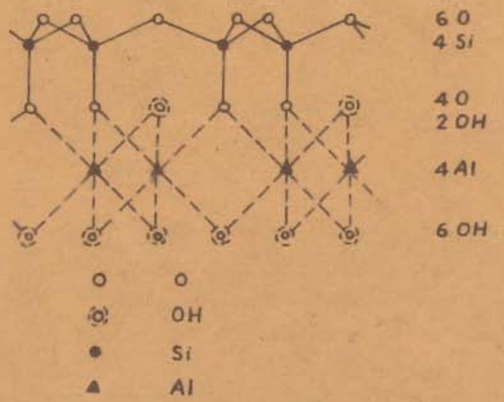
b. Structure of montmorillonite:- The mineral was first studied by Le Chatelier(40) and has been assigned the formula $(OH)_4 Al_4Si_8O_{20} \times H_2O$. Ross and Hendricks(41) established the identity of montmorillonite as a definite clay mineral species. Structurally, the mineral consists of three layers,a gibbsite sheet enclosed between two silica sheets with their vertices pointing towards each other and towards the centre of the unit. X-Ray studies have shown stacking of silica-alumina-silica units in the c-direction, layers being continuous in a and b directions. Water and other polar molecules can easily penetrate,between the unit layers,causing the lattice to expand in the c-direction. Marshall (42) and Hendricks (43) showed that montmorillonite always differed from its theoratical formula,because of



The chlorite structure projected on 010. In this projection, O & (OH) ions overlap and their distribution in the b direction cannot be shown.



Atom arrangement in the unit cell of a three-layer mineral (Schematic)



Atom arrangement in the unit cell of a two-layer mineral (schematic) substitutions within the lattice of Al by Mg,Fe,Zn,Cr etc. and of Si by Al or P,giving a series of group minerals. Opinions have,however,differed as to the correctness of the structure proposed by these workers. Edelman and Favejee (44) and McConnell (45) have suggested revised structures, particularly in view of the large c.e.c. of the mineral.

c. Structure of illite:- The name illite was proposed by Grim et al (46) for the mica like minerals,with a 10 A c-axis spacing,which shows substantially no expanding lattice characteristics. The structure of illite group of minerals follows the pattern suggested by Pauling(loc.cit.), Jackson and West(47) and Hendricks and Jefferson(48). The basic structure of illite species is very similar to that of montmorillonite,with the difference that some of Si^{+4} is replaced by Al^{+3} and the resultant charge deficiency is balanced by K^{+} ions between the silica sheets of two successive units. In fact the K^{+} ions act as bridges binding the unit layers together,so that these donot expand in presence of water;structural formula of the mineral is given as $(OH)_4K_x(Al_4Fe_4Mg_4Mg_6)(Si_{8-y}Al_y)O_{20}$.

d. Structure of chlorite:- The chlorite field is, customarily,divided into two broad subdivisions,the orthochlorites with compositions ranging between$(Mg,Fe^{+2})_4Al_2(Si_2Al_2)O_{10}(OH)_8$ and $(Mg,Fe^{+2})_6Si_4O_{10}(OH)_8$,with minor amounts of other elements,and the leptochlorites which do not fit into this scheme and are generally richer in trivalent ions,notably Fe^{+3}. In many cases the latter appear to have originated as ferrous orthochlorite and to have been subsequently oxidized,(49).

The chlorite structure consists of an alternating series of brucite-like-hydroxide layers of general composition $A_3(OH)_6$ and mica like layers, of general composition $B_3(Si,Al)_4O_{10}(OH)_2$; A and B stand for a variety of ions in octahedral positions which, in orthochlorites are mainly divalent. If there are $(Si_{4-x}Al_x)$ atoms in tetrahedral positions the layer acquires a negative charge(-x)which is balanced by a corresponding number of trivalent ions in the A and B positions. On a-priori grounds it is not evident whether the distribution of cations in A and B positions is the same and whether the charge is balanced wholly in the mica layer or in both the layers. The following subdivisions, according to chemical compositions, are based on the work of Hey (49), Orcel(50), Orcel et al(51), Winchell(52,53) and Brindley and Gillery(54), who have also given a relation of optical properties to its chemical composition.

Case 1. Orthochlorites:- Simplest situation arises when the A and B sites are occupied by the same distribution of cations, and Al is the only trivalent ion. Composition and charges of the layers are as follows:

Brucite like layer $(A_{3-x/2}Al_{x/2}(OH)_6)^{+x/2}$,

Mica like layer $(A_{3-x/2}Al_{x/2}(Si_{4-x}Al_x)O_{10}(OH)_2)^{-x/2}$,

Total composition $A_{6-x}Al_x(Si_{4-x}Al_x)O_{10}(OH)_8$ ....(1).

Case II. Orthochlorites containing Mg^{+2} and Fe^{+2} ions:- If in formula(1), A_{6-x} contains y Fe^{+2} ions and the remaining ions are Mg^{+2}, the formula becomes

$Mg_{6-x-y}Fe_y^{+2}Al_x(Si_{4-x}Al_x)O_{10}(OH)_8$ ....(2).

Case III. Orthochlorites containing Fe^{+3} ions:-In orthochlorites, Fe^{+3} is usually a minor constituent and probably occurs wholly in octahedral positions. Osthaus, (55), have shown the possibility of Fe^{+3} ions occupying tetrahedral positions, but if the usual assumption is made that they occupy octahedral positions, then the formula can be written as

$$Mg_{6-x-y}Fe^{+2}Fe_{z}^{+3}Al_{x-z}(Si_{4-x}Al_{x})O_{10}(OH)_{8} \text{ ....(3).}$$

Case IV. Leptochlorites:- These are oxidized chlorites as shown by Hey (loc.cit.) formed by a process of the type

$$Fe^{+2}+OH^{-} = Fe^{+3}+O^{-2}+H$$

where H leaves the lattice as H_2O by aerial oxidation. Here Fe^{+3} ions do not replace Al^{+3} ions in octahedral coordination. The leptochlorite formula can be written as

$$Mg_{6-x-y}Fe_{y-z}^{+2}Fe_{z}^{+3}Al_{x}(Si_{4-x}Al_{x})O_{10+x}(OH)_{8-z} \text{ ....(4),}$$

where z is the number of ferrous ions which have been oxidized to ferric ions. The formula represents a partially oxidized orthochlorite of type II. When the original mineral already contains some ferric ions, as in formula III, a more complex leptochlorite formula is required.

Case V. Chlorites with unequal distribution of octahedral cations:- A possibility not usually considered mainly because it is not amenable to bulk chemical analysis, is that the octahedral ions are not distributed equally between the A and B positions. It is conceivable, for example, that the replacement of divalent by trivalent cations required for electrical neutrality may occur wholly or largely within the mica-like layer. Such a structure would have little or no ionic binding force between layers and would be expected to resemble talc as regards mechanical properties.

Another possibility is that a chlorite may be formed from a mica by replacing the interlayer cations by a hydroxide layer carrying the same overall ionic charge.The ions occupying the A and B sites may then be of different compositions. If Fe^{+3} ions are absent the composition becomes

$(Mg_{6-a-b-x}Fe^{+2}_{a+b}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8$ ....(5),

where $x = x_1+x_2$,and charges are ,

Brucite like layer$(Mg_{3-a-x_1}Fe^{+2}_aAl_{x_1}(OH)_6)^{+x_1}$,

Mica like layer $(Mg_{3-b-x_2}Fe^{+2}_bAl_{x_2}(Si_{4-x}Al_x)O_{10}(OH)_2)^{-x+x_2}$.

Case VI. Chlorites with diocatahedral layers:- A further possibility is that one or both of the octahedral layers in a chlorite structure may be dioctahedral rather than trioctahedral.Possible combinations are

a. $(Mg_{3-x}Al_{2+x})\ (Si_{4-x}Al_x)\ O_{10}(OH)_8$,

and another possibility of double dioctahedral case is

b. $Al_{4+x/3}(Si_{4-x}Al_x)\ O_{10}(OH)_8$.

<u>Physico-chemical properties of clay minerals:</u>

The clay particles,in water,appear to exist in the form of a very complex ion(negative),exposing a highly negative surface,comparable to the inner part of the double layer,the outer layer being made up of a swarm of rather loosely held cations surrounding the particles. When such particles are dispersed in water,the cations get hydrated and dissociate leading to the formation of a diffused double layer and thus can be compared to a dissociated electrolyte.

No doubt, the charge on the clay particles exerts an important influence on their properties; the larger influence of the factors, like adsorption, hydration, pH etc. makes them lie intermediate between the lyophobic and lyophilic colloids. The following physico-chemical properties are worth attending to:

1. Ion exchange:- Exchange of both cations and anions is possible in clay suspensions and anion exchange is negligible, in many cases, in comparison to cation exchange. Since the replacement of ions and subsequent occupying of exchange sites by the ions added is dependent on their relative adsorbability, ionic adsorption plays the most important part in this cation exchange phenomenon.

Valency and hydration of ions are the most important factors in determining the energy of adsorption and release. Wiegner and Jenny(56) have over emphasized the influence of hydrated ions on replaceability. Controversy, however, exists as far as the feasibility of the hypothesis on hydration of ions is concerned. Bernal and Fowler(57), Bar and Tenderloo (58) and Baver(59) etc., have presented data that do not fit in with cation hydration view point. Recently Hendricks (60), after careful dehydration studies, have shown that Na^+, H^+, K^+ and trivalent ions are not hydrated when adsorbed by clay minerals, while Ca^{+2}, Ba^{+2}, Mg^{+2} and Li^+ undergo hydration. Replaceability is also related to polarization(58) and also to the temperature, (61). Gieseking and Jenny(62), Jarusov(63), Bar and Tenderloo(58) and Schachtschabel(64) etc., have demonstrated that there is no single replaceability series characteristic of all clay minerals,but there is a separate replaceability series for the various clay adsorption complexes. The size of the exchanging cation,also,controls the exchange phenomenon(65),ions of smaller ionic radii are easily replaced by ions of larger radii,a striking exception to this rule being of K^+ ions,(66).

Mattson(67),Ravikovitch(68),Toth(69) etc.,have shown that many clays exhibit anion exchange reactions,possibly in the following three ways,(i)replacement of OH^- ions, McAuliffe(70),(ii) ionic adsorption of phosphate,(71),(iii) exchange reaction through definite spots which may be considered as anion exchange spots, as shown by Schofield(72).

2. Stability of clay suspensions:- Like hydrophobic colloids, the zeta potential controls the stability of the clay suspensions. Jenny and Reitemier(73)observed,that the energy of adsorption determines the potential of the particle and consequently the stability of the suspension. Potential depends upon valency and hydration. According to Wiegner(74) stability of the clays varies with the nature of adsorbed ion and follows the Hofmiester series. The Schulze Hardy rule for the flocculation of clay suspensions is,only approximately,followed,since the minimum electrolyte requirement varies with the pH,the nature of the adsorbed cations and concentration of the suspension,(74).

3. Cation exchange capacity(c.e.c.)of clay minerals:-According to Kelley (75) who reviewed the history of cation exchange in details,the discovery,that soils and clays have

the power of exchanging cations with solutions, containing other cations, was the outgrowth of observations dating back into remote past. Exchange capacity is measured in terms of milliequivalents (m.e.q.) per 100 g. of clay. Consideration of the factors influencing c.e.c. shows that there is no single value which is characteristic of a given group of clay minerals. Since the c.e.c. of a given mineral type may vary with so many factors, capacity values are rigorously comparable, only, if they have been obtained by the same standard procedure.

Causes of cation exchange:

1. Broken bonds, around the edges of the silica, alumina units, would give rise to unsatisfied charges, which would be balanced by adsorbed cations. In kaolinite and halloysite, broken bonds are the major cause of exchange capacity. Similarly in illite or chlorite this is an important cause of c.e.c.. In montmorillonite only about 20% of c.e.c. is due to this reason.
2. Substitutions within the lattice structure, of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet, and of ions of lower valency particularly magnesium for trivalent aluminum in the octahedral sheet, is the main cause of exchange capacity of montmorillonites.
3. The hydrogen of exposed hydroxyls may be replaced by a cation which would be exchangeable and is an important cause of exchange capacity for kaolinite and halloysite.

Determination of cation exchange capacity and exchangeable cations:

Literally, dozens of methods have been suggested for this purpose. Kelley (75) and Peech et al (76) have considered in details the various methods and have pointed out their pitfalls.

A. Chemical methods(Analytical):- Measurement is generally made by saturating the clay with NH_4^+ or Ba^{++} ions and determining the amount held at pH 7.0. In the absence of water soluble or slightly soluble salts and for a clay mineral which itself is not moderately soluble, the determination is not very difficult. However, in the case of degraded clays, like illite or chlorite, it is difficult to separate exchangeable from non exchangeable ions. Also in acid clays the presence of Al^{+3} ions, or in ferruginous clays the presence of Fe^{+3} ions tends to partially clog some of the exchange positions and make the c.e.c. determination very difficult, (2). The problem is particularly difficult for clay minerals of relatively high solubilities.

The exchangeable bases are removed either by electrodialysis or by leaching the soil on a filter paper by a salt solution or a dilute acid. Kelley and Brown(77)determined the exchangeable bases obtained by leaching the soil with solutions of ammonium chloride and hydrochloric acid of different concentrations and showed that nearly the same quantities of calcium, magnesium, potassium and sodium were replaced from a particular soil. Leaching agents used by Hissink(78) are normal solutions of ammonium chloride, potassium chloride and sodium chloride. Use of ammonium acetate as a leaching agent was proposed by Schollenberger(79). The method of leaching the soil with acetic acid solution was described by Williams(80).

Different methods have also been described for the determination of exchangeable hydrogen of the clays, by Hardy and Lewis, Crowther and Basu and Parker; a good description of these is given by Wright(81).

B. Flame phtometric determination:- The flame emission technique is a rapid and sensitive method, for the determination of c.e.c. of the soil or clay. Measurements with K, Na, Ca, Ba, Cu, Mn, and other ions have all been adapted to the flame emission determination. The saving in time over titrimetric, colorimetric or gravimetric determinations is considerable. In each case the c.e.c. determination consists of saturation of the exchange charges with one of the above cations, removal of the excess soluble salt by leaching with alcohol and then displacement of the exchangeable cation by means of a solution of a second saturating cation,(82).

C. Polarographic determination:- The use of manganous ions for the replacement of the exchangeable clay cations was suggested by Bower and Truog(83). A method, for determining manganous ion concentration, is by the use of polrographic analysis; the requirement for this method is a replacing cation reducible at the dropping mercury electrode, and this cation should be replaceable from the clay by a second cation that has a greater half wave potential. Since the solution furnishing the second cation can be used as the supporting electrolyte and manganous ions produce a good polarogram in alkali chloride supporting electrolytes(84), the polarograms of the leached manganese in potassium chloride medium are studied(85).

Chemical analysis:

A vast number of chemical analysis of clay materials have been published. Objective has been to show the spread of the composition of the various clay minerals. Grim(86) has given a relation of composition to the properties of clay minerals. Chemical analysis of substances and reaction products, have been used in correlation with D.T.A. by Caillere and Henin (87) who analyzed chemically their synthesized antigorite, and discussed its relation with thermal properties. Others who have vastly deduced the relationships between physical, chemical and thermal properties of clays, on the basis of chemical analysis are Vicente and Verduch(88), Stegmuller(89) and Orcel(50). A good deal of analytical data on reference clay minerals is published by the American Petroleum Institute (90).

Thermal properties:

A. Dehydration:- It involves the loss of any water, adsorbed, interlayer, or lattice OH water, held by the clay minerals. A study of dehydration is concerned with the amount of water lost, rate of water loss, temperature of dehydration etc.. Dehydration frequently involves significant changes in the structure of clay minerals and consequently changes taking place during the heating of the clay minerals cannot be considered apart from dehydration. In the method of dehydration, the loss in weight of the material upon heating to higher and higher temperatures, is recorded and plotted against the temperature. The sample may be heated at a given temperature until no loss in weight occurs; it is then heated to a higher temperature and held at that temperature until no loss in weight takes place. This procedure is repeated until a temperature is reached at which there is no further loss in weight. This is the recommended procedure by Nutting (91), Ross and Kerr (92), Kelley (93) and many others(41,46). Various investigators have plotted their data differently,(2). Nagelschmidt (94) has pointed out,that it is generally assumed,that the loss in weight of one mineral upon heating is not affected by the presence of a second mineral and that the dehydration curve of a mixture would be equal to the superposition of curves of the separate minerals in the mixture. The loss in weight can also be due to the loss of carbondioxide from carbonates and the loss of volatile constituents. Also the oxidation of ferrous or manganese tends to increase the weight. Factors like grain size, crystallinity,nature of adsorbed ions etc.affect dehydration results.

B. Differential thermal analysis(D.T.A.):- The method of differential thermal analysis determines,by suitable apparatus, the temperature at which thermal reactions take place in a material,when it is heated continuously to an elevated temperature and also the intensity and general character of such reactions. In case of clay minerals,D.T.A.,shows characteristic endothermic reactions due,to dehydration and to loss of crystal structure and exothermic reactions due to the formation of new phases at elevated temperatures. It is applicable to any material,which experiences thermal reactions on heating,which begin abruptly and are completed in a relatively short temperature interval,like the metal hydroxides. D.T.A. results are plotted in the form of a continuous curve, in which the thermal reactions are plotted against furnace temperatures. LeChatelier(95) was the first person to use this technique. In 1899 Roberts-Austen (96) devised the differential thermocouple method of measuring temperature differences, which was later modified by Burgess (97). Excellent reports of Orcel (98) and Orcel and Caillere (99) emphasized clearly the applicability of the method to clay mineral researches and since that time it has been used in the study of clays by many different investigators(100).

X-Ray analysis:

Clay minerals exist for the most part only in very fine clay particles and thus the powder method is usually used to obtain the diffraction data. Because of certain inherent characteristics, of the clay minerals, special cameras and special techniques are frequently required for clay mineral work. Brindley (101) has recently considered X-Ray methods as applied to clay mineral researches after the work of Bragg(102), Buerger(103) and others.

In clay minerals there are few, if any, reflections obtained from spacings less than 1 KX. The first order basal reflections of the clay minerals are frequently their most important reflections, corresponding to spacings as large as 20-30 A and for this reason cameras with diameters of 9-20 cms. are commonly employed in clay mineral work.

Most of the clay minerals occur in flake shaped units and consequently when a powder is packed an aggregate orientation of the flakes developes readily. Bradley et al (104) have described a method of forming well oriented aggregates and using them in X-Ray diffraction studies.

In case of montmorillonites and vermiculites proper control of the humidity of the atmoshpere within the camera is essential. Imperfections of crystals affect their diffraction characteristics and are particularly important for clay mineral work. Shape and size of the crystal particles,exposed to X-Rays,influence the diffraction effects.

Kaolinite group gives the prominent basal reflections at about 7.14 KX(001) and 3.57 KX (002) which are usually adequate for its identification. The third order peak at 4.7 KX is seen to indicate the presence of chlorite. Treatment of a sample of montmorillonite with ethylene glycol provides a sharp (001) reflection at 17 KX.

Infrared spectra of clay minerals:

Atoms which are grouped together in molecules,do not remain at rest, but are continuously in vibration. Such vibrations produce periodic displacement of atoms with respect to one another,causing a simultaneous change in interatomic distances. The frequencies of the vibrations fall within the range of 10^{13} to 10^{14} cycles per second,which is of the same order of magnitude as the frequencies of infrared radiations. Vibrations which are accompanied by a change in dipole moment give rise to the absorption of radiations in the infra red region,of the electromagnetic spectrum. Several modes of vibrations may occur,for a particular atomic group,each at a characteristic frequency and normally independent of other modes.

If molecules of a substance whose vibrations are accompanied by a change of dipole moment are irradiated,by a succession of monochromatic bands of infrared,those radiated frequencies which correspond to the intramolecular vibrational frequencies may be absorbed wholly,or in part. If the percent of radiation which is absorbed by a substance is plotted against the incident wavelength (or frequency) the ensuing graph may be interpreted in terms of the intramolecular vibrations.The graph,therefore,will be characteristic of the material and can be used in its identification. In addition it should also provide data on the structure and bonding characteristics within the molecules.

Keller and Pickett(105,106) and Kerr and collaborators (107) are the pioneer workers,as regards the application of infrared spectroscopy to clay mineralogy. Development of the commercial infrared spectrometer combined with improvement in standard instrumentation,has resulted in improved adaptability to individual research needs,with a wide spread increase in its possibilities of applications. Present equipment makes possible the focus of infrared spectroscopy on mineralogical problems. Of major significance is the knowledge that a number of molecular groups such as CO_3'',SO_4'',NO_3' and OH' have characteristic infrared spectra,which may be rapidly detected in an unknown sample.

In the case of clay mineral investigations,wavelengths of 2-15 microns are used,since the characteristic spectra occur in this range. Early work was done by mounting the clay in an oil medium(usually Nujol) which caused difficulty,by adding its own spectrum to that of the clay. Techniques have been developed for mounting the clay without any additive,but special arrangements are required for such studies.

The graphs obtained by different investigators for the same clay,clay mineral samples have the same general characteristics,but show considerable variations in details. Further investigations are required to show which of these minor features of the curves are significant and which are spurious and due to factors of technique.

Clay minerals-organic reactions and staining tests for clay minerals identification:

Mattson (108) has demonstrated a reduction in c.e.c., by complexing clays with proteins and similarly Smith (109) reacted organic bases and their salts with montmorillonites and presented evidence that the reaction was one of ion exchange. Mattson(loc.cit.) believed that adsorbed proteins might be more resistant to microbial decomposition,than free proteins.

And out of the many analytical techniques for characterisation of clays based on clay mineral organic reactions i.e., X-Ray techniques,D.T.A.,stain tests,optical methods,surface area determination etc., the method of stain tests is the most simplest and quickest of all.

Faust (110) has reviewed the history of staining techniques,in general,and has summarized much of the early work. Behrens (111) was the first to have applied staining methods to mineralogy. An extensive literature has now grown up regarding the use of staining methods and many persons have attempted to apply them to clays.

Adsorption of various organic substances by natural and chemically altered or heat treated clays can produce colour changes in the clay. Frequently, such changes vary, depending on the identity of the clay mineral and its composition. The colour changes, therefore, provide a possible basis for identifying the clay minerals.

In general the reaction and the resulting colour change are slight or absent for clay minerals of low adsorptive capacity, such as kaolinite, but are pronounced for highly adsorptive clay minerals, like montmorillonites. Two mechanisms have been proposed to explain the colour reactions obtained with clay minerals and various reagents, (1) an acid base reaction in which the natural or acid treated clay reacts as an acid and (2) an oxidation reduction phenomenon in which certain ions, mainly ferric ion, contained in the clay mineral lattice, cause an oxidation of the reagent. Substances causing colour changes by the acid base reaction include triphenylmethane, azine and azo dyes. Substances, probably, changing the colour of clays due to oxidation reduction reactions include benzidine and other aromatic amines.

Identification of clay minerals by electrometric titrations:

Bradfield's (112) experiments marked the beginning of electrochemical investigations on clays. It was shown that acidic clays were in some way analogous to weak acids in solution and could be titrated with bases to fairly well defined ~~and~~ end points. Work of Mukherjee and coworkers (113) bears enough testimony to this fact.

Both potentiometric and conductimetric titrations of H-clays may be employed for characterisation of clay minerals, as initiated by Paver (115), Scarseth (116), Denison(117) and Marshall (118) etc..

How far the methods of these electrometric titrations, have been successful in investigating the properties of clay minerals, is difficult to assess. Mital and Bhatacharya (119) and Davis (120) have drawn attention to factors, like existence of non equilibrium conditions, retardation effects due to exchangeable aluminum etc., during these titrations. Singhal and Malik (121) have recommended the use of non aqueous medium, for these electrometric titrations, to get a more precise idea about the dissociability of different acid groups in clay minerals and their identification.

Characterization of clay minerals from rheological properties:

Viscometric studies have been extensively employed in determining the behaviour of clay minerals. The theoratical concepts, of Einstein (122), Smoluchowski (123), Norton(124), Baker (125), and Currie (126), to explain the viscosity of colloids, can also be applied to study these clay dispersions. Clay suspensions, inspite of their large dependance on charge and zeta potential, for their stability, show a fairly high degree of hydration, responsible for, properties like thixotropy, rheopexy, dilatancy etc.. All these, in turn, may contribute to viscosity variations to such an extent that useful information on the nature of the clays can be obtained from the viscosity data.

A novel and useful line of attack in the study of viscosity of clay suspensions can be to investigate the influence of Hofmeister series of ions on the viscosity of clay colloids. The view point of Singhal and Malik,(127) that both pH and ion of the Hofmeister series,exert a combined influence on the viscosity of clays,is worth considering. These authors have put this information to use in identifying clay minerals.

Wiegner-Pallmann suspension effect:

For the first time Wiegner (128) drew attention,to the importance of different types of potentials viz.,electrochemical,Stern and Guoy etc., existing in clay suspensions, due to the electrical double layer,associated with the clay particles. The electrochemical potential,which may be given in terms of pH,pAg,pCl etc., depending on the system employed, and its precise determination can be of some value in determining the nature of the clay minerals. For example,when a sol or suspension is in equilibrium with a particle free solution,then the pH determination can be carried out in four different ways. The hydrogen electrode may be situated in the suspension or in the equilibrium liquid and similarly the salt bridge (or the reference electrode)may also be brought into contact with either of these two. The position of the hydrogen electrode is without any influence,on the potential measured,but the position of the salt bridge makes a difference. Usually the electrode connected to the salt bridge shows a lower potential,when the salt bridge is in contact with the suspension,than when it is in contact with the equilibrium solution;this is particularly so when the suspension is negatively charged.

The effect described above has been extensively investigated by Pallmann and Wiegner(129) who determined the pH in suspensions of clays,permutites, $Fe(OH)_3$, $Al(OH)_3$ and di and tri calcium phosphates. De Bruyn (130) found the same effect in the determination of the pI of concentrated negatively charged AgI sols. A change in e.m.f.similar to this "suspension effect" was also noticed by Loosjes (131) while placing a liquid junction alternatively in a capillary and in a wide tube. Qualitatively these effects are easy to understand. A rigorous quantitative treatment is still lacking though Pallmann (132) has given an equation, $C_H = C_H o + K$, where C_H is the concentration of H^+ ions of the dispersion, $C_H o$ is the concentration of the H^+ ions of the medium and K is a constant. This equation is followed upto medium concentration of the dispersion beyond which the curves bend towards the X-axis.

Although Augusta Unmack (133) has refused to accept the existence of suspension effect but the data by Wiegner (128), Pallmann(132), Gatovskaya and Vasilev (134),Nikolskii(135), Sollner (136),Overbeek (137),Bloksma (138) and Voiteskhovskii and Vovnenko (139), support not only the existence of this effect,but have also given several empirical relationships between pH and concentration of the sol. From these data it is clear that sol concentration effect (or suspension effect),is not small enough to be neglected. The difference in pH for the infinitely dilute and a concentrated solution amounts two two units of pH,in many cases of the clay sols investigated.

Pallmann (132) has ascribed the suspension effect,to a strong adsorption of H^+ ions,its intensity decreasing with decreasing density of the adsorbed layer. There is,however, now much evidence, by the work of Jenny (140), Peech (141), that the difference in e.m.f. manifests itself, through the junction between the suspension and the KCl of the salt bridge, employed in the calomel electrode. According to Overbeek (137), the difference in the e.m.f., results from the fact that the transference numbers of the ions in the suspension, differ from those in the equilibrium solution, the difference being due to the presence of charged particles and the excess of ions in the double layer surrounding them. Overbeek (loc.cit.) proposed an approximate equation, for calculating the magnitude of the effect, when a saturated KCl bridge is employed. As predicted by him, the magnitude of the suspension effect has been found, by Bower (142), to vary in an orderly manner with the electrolyte concentration and the exchangeable sodium percentage of the soil suspension.

Very recently, Singhal and Malik (143) have made an attempt to use Pallmann effect as a possible guide for characterization of clay minerals. The pH difference of the equilibrium liquid and the suspension, in acid medium, for a particular clay concentration was found to be constant and followed the order, montmorillonite > Kaolinite > illite. This pH difference, when plotted against the concentration of the clay, showed a uniform decrease in the case of montmorillonite and a gradual increase in case of kaolinite.

Polarographic behaviour of clay minerals:

It is well known that every reduction takes place at a definite voltage, which is characteristic of the substance employed. If the voltage of the electrolyzing current is lower than the reduction potential, no reduction takes place, and consequently no current passes through the solution. When the requisite potential is reached, the current flowing through the solution is directly proportional to the concentration of the reducible substance. This technique, known as polarography, has been very widely used in analytical chemistry and chemical technology etc..

A review of the existing literature would reveal that no work has been done, so far, on the polarographic behaviour of clay minerals. The field of clay mineralogy, precisely speaking, is not the only one to which this technique has not been applied. Before 1950 there is no reference of any work on the polarographic behaviour of suspension, and very few, if any, references are available on the polarographic behaviour of colloidal solutions. Micka (144) was the first to apply this technique, to study the individual behaviour of suspensions of sulphides, selenides, hydroxides etc..

Although polarography had always been considered, to be a method applicable only to substances in solutions, it is now being realised that some solid materials may also be determined using this technique. Micka(loc.cit.) suggests the use of materials in a highly subdivided state, with constant stirring, to put polarography to some profitable use in the study of such cases. He has further shown that fresh precipitates such as sulphides of lead and mercury gave good current voltage curves, with a sharp and reproducible maximum.

The potential at which the current was a maximum was characteristic of the precipitate and was reproducible to ± 20 mv. It has also been stated by him that strong adsorption on the electrode surface is necessary for this type of reproducible reduction characteristic of the precipitate used.

Earlier to this, Puri, and Hoon (145), probably in a bid to determine the c.e.c. of the soils, did some work on the current voltage curves of soils saturated with different cations, and compared these current voltage curves with those of chlorides of Na, K, Li, NH_4, Ca, Ba and magnesium. Curves with these salts and the corresponding "soil saloids" were exactly similar. Puri (12) deduced the close analogy between "saloids" and soluble salts. Based on these studies he put forward the idea that exchangeable cations in soils exist in chemical combination and not in an adsorbed state. In the absence of much practical details of the method employed by Puri (loc.cit.), it is difficult to conclude anything about the polarographic behaviour of the soils.

Oxidation reduction potentials in clay minerals:

The idea of the existence of redox potentials, in clay suspensions, had not been put to much use so far. It is, however, worth mentioning the underlying principles involved therein: The fundamental equation involved in oxidation-reduction potentials is

$$E_h = E_o - \frac{RT}{nF} \ln \frac{(Red)}{(Ox)}$$

where E_h is the potential, referred to the normal hydrogen electrode as zero, of the system under consideration, E_o is a constant characteristic of the system and equal to E_h when

(Red)/(Ox) is unity.(Red) and (Ox) represent the concentration of reductant and oxidant respectively and R,T,n and F have their customary significance. The equation shows E_h to be dependent on the ratio of the oxidant to reductant,which is the most important factor in this thermodynamic relation. Wherever a definite potential difference is to be established at the electrode,there must be in the system two species, one of which is the direct or indirect reduction product of the other,and the ratio of their concentration or activities must be of finite magnitudes. Some potential will always be developed,when a clean platinum electrode is dipped into a clay suspension,but unless the thermodynamic equation can be satisfied by the introduction of some known components,the results will have no fundamental value and may be misleading.

The presence of iron,in majority,if not all,clay systems might reasonably be assumed and all potentials interpreted in terms of the system $Fe^{+3} + E \rightleftharpoons Fe^{+2}$,Puri (12). The possibility of the participation of other systems, in dealing with a material like a clay mineral,may not be ruled out. The results in this case can be valuable and interpretable,only if characteristic data for one particular system,can be obtained,which preclude interference by another system. The linear relation between pH and E_h has been shown for a system in which the ratio (Red) / (Ox) is constant.In clays and soils the only possible system,which gives a constant potential for a given ratio,irrespective of the pH value,is that of Fe^{+3}, Fe^{+2}, but the pH range of this system is limited, which is almost never found in naturally occuring clays and soils, leading to the conclusion that this system plays no part in determining the oxidation reduction potentials in soils and clays. However, by eliminating extraneous influences, it might be possible to interpret these oxidation reduction potentials in terms of some other known system.

Aim of the present investigation:

As mentioned above, different methods have been given for the transformation of montmorillnite structure to chlorite structures but the formation only of magnesium and aluminum chlorites has been confirmed, (33). With this main aim of checking and confirming the transformation of montmorillonite to ferric chlorite and nickel chlorite the present investigation was undertaken.

This study includes the identification of such structures by methods like (a) X-Ray diffraction analysis, (b) Differential thermal analysis, (c) Infrared spectroscopy, (d) Dehydration curves, (e) Chemical analysis, (f) Cation exchange capacity determination by various techniques, (g) Electrometric titration methods, in aqueous and non aqueous media, (h) Viscosity measurements and the effect of pH and the lyotropic series of ions and (i) Pallmann effect study etc..

Work on polarographic behaviour of clay suspensions has been initiated for the first time and as will be seen in the pages ahead a new approach for the identification of various clay minerals is presented.

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CHAPTER I

Preparation, analysis and identification of transformed montmorillonite structures (chlorites).

INTRODUCTION

Structure of chlorites:

Chlorites are a group of clay minerals which are structurally related to the three layer clays. In these minerals, the charge compensating cations between montmorillonite-type unit layers,are replaced by a layer of octahedral magnesium hydroxide. Owing to some replacement of magnesium by aluminum in the brucite layer,this layer has a net positive charge. Since the cation exchange capacity of chlorites is very low,the positive charge of the brucite layer compensates the net negative charge of the unit layers.

Formation of chlorites:

The widespread occurence of varieties of chlorites in soils and sedimentary rocks has been frequently explained as the result of the precipitation of hydroxides of magnesium, iron or aluminum,between the unit sheets of expanding clay minerals. This explanation has been supported by reports of the laboratory preparation of ~~chlorites~~chlorite-like-materials,as a result of the precipitation of hydroxides in montmorillonite suspensions. The original description of this process was given by Caillere and Henin(29,30),Longuet-Escard(31) and Youell(32) who have prepared complexes of montmorillonite with the hydroxides or hydrous oxides of magnesium, aluminum,nickel,cobalt,zinc and ferrous iron.

In these investigations the method of Slaughter-Milne(33) was followed for the preparation of these montmorillonite-metal hydroxide complexes. Slaughter-Milne (33) have confirmed the formation of some of the chlorite structures from these complexes by X-Ray diffraction studies.

Dehydration studies:

Nutting(91) has presented some dehydration curves for several chlorites. All of Nutting's (91) curves for the chlorite minerals show very little water loss prior to about 500°C and a sharp loss of water between 500° - 550°C. The curves above 600°C show considerable variation, some of them show a gradual continuous loss of weight from 600° - 850°C, whereas others show a relatively slight loss between 600° - 800°C and then a relatively abrupt loss from 800° - 900°C. The method of Nutting(91), Ross and Kerr(92) and Kelley(93) was followed to study the dehydration curves of these transformed montmorillonite structures.

Differential thermal analysis studies:

Orcel(146), Orcel and Renaud(147), Barshad(148) and Grim(2) have obtained differential thermal curves for a large number of chlorite samples. The samples studied by them show no low-temperature endothermic reactions, indicating the absence of interlayer or adsorbed water. All the samples exhibit a distinct sharp endothermic reaction between 500° - 700°C. Most of them show a second endothermic reaction at about 800°C and this peak is followed by a sharp exothermic peak. Orcel(146) concluded from his work that the hydroxyl water of the chlorites is driven off in two stages. Nutting's (91) dehydration curves also show that the chlorites, he investigated, lost their OH water in two stages. The smaller particle size of the chlorite clay minerals and, possibly some defects of orientation of layers, would, perhaps, permit the loss of some of the OH water of the brucite layer sheet at a relatively lower temperature. Brindley and Ali(149) presented differential thermal curves for some chlorites but were unable to correlate the thermal reactions in each case with the phase developed, as shown by their X-Ray diffraction analysis, probably, because the new phases develop slowly and / or involve only a very slight structural shift so that it would not be accompanied by an intense or sudden energy change and consequently no thermal reaction would be expected on the differential thermal curve.

Exchangeable cations:

Study of cation exchange includes the determination of total exchangeable cations (or also known as exchangeable cation content, Hissink's S), the exchangeable hydrogen and the cation exchange capacity. Cation exchange capacity is the sum of total exchangeable cations and the exchangeable hydrogen. Total exchangeable cations were determined by replacement with neutral N ammonium acetate solution, following the method of Bray and Willhite(150). Exchangeable hydrogen was estimated using the third method of Parker(151) of leaching the soil with Barium Acetate.

Flame spectrophotometric studies:

Recent development of refined instruments for direct flame spectrophotometry offers the possibility of shortening the time of soil analysis. Myers, Dyal and Borland(152) have established conditions, considered satisfactory, for estimating exchangeable potassium in soils by flame spectroscopy. Toth and Prince(153) have given a procedure for exchangeable calcium,potassium and sodium by direct photometry of flame emission from soil leachates. In case of Toth and Prince (loc.cit.) the procedure is much elaborate and a rapid method for total exchangeable cations has been given by Pratt and Bradford(154) and also Fieldes et.al.(155). The results obtained by flame spectrophotometric analysis are comparable with the values obtained by volumetric or gravimetric analysis. This method is considerably faster than the usual chemical methods and the interfering elements can be easily removed. The method described by Fieldes et.al.(155) has been used in the present investigation.

Polarographic estimation:

The accepted procedures,Wiklander(156),for determining total cation exchange capacity involve replacement of the exchangeable soil cations by a cation in a leaching solution, removal of excess of electrolyte by washing and subsequent removal or quantitative determination or both of the replacing cation. Sodium or ammonium ions are generally used to saturate the soil,however,the use of manganous ions for replacement of the exchangeable soil cations has been suggested by Bower and Truog(~~20~~83). A method,other than colorimetric,for determining manganous ion concentration is the use of polarographic analysis. Since manganous ions produce a good polarogram in alkali chloride supporting electrolytes,Kolthoff-Lingane(84), and when adsorbed by soil can be replaced by potassium in solution,manganous ion,as manganous chloride was used to replace the exchangeable soil cations. Potassium chloride was used to replace the manganous ion and to act as a supporting electrolyte during the subsequent polarographic determination of the manganous ion concentration. A similar method was given by Manuele(85),but Holtzinger et.al.(157) have given a modified form of the method. Another cation i.e.,zinc as zinc chloride has been tried for this purpose and the two results compared. Zinc gives a well defined reversible wave in potassium chloride though at a very low concentration of zinc the wave tends to be ir-reversible. Results with mangan~~ous~~ese as the replaceable cation have been correlated with those of zinc.

Chemical analysis:

The chlorite clays so obtained from the transformation of the montmorillonite structure were subjected to their chemical analysis,i.e., estimation of silica,alumina,magnesia and other cations associated with them. Whenever possible the data of chemical analysis was supplemented by the results of physico-chemical methods. Chemical analysis can be a good test of the composition of a clay mineral and the substitutions in the octahedral or tetrahedral sheets can be confirmed. Slaughter and Milne(33) have made a calculation of the quantity of brucite,$(Mg(OH)_2)$,that can be introduced between unit sheets of montmorillonite to yield chlorite like structure and have shown it to be approximately 16 m.e.q. per gm.of pure clay. The same calculation is applicable to the aluminum hydroxide precipitate if the gibbsite structure is assumed.

X-Ray analysis:

McMurchy(158) and Brindley and Robinson(101) gave ~~a~~

the X-Ray diffraction data for many of the naturally occuring chlorite minerals. The variations from one chlorite to another are to be found in slight modifications of intensities or lattice spacings,due to small variations of unit cell dimensions. The small size of the chlorite particles and their less regular crystallinity causes some diffuseness of reflections and the absence of some ordinarily weak reflections. Most chlorites give a clear sequence of four or five basal reflections from the 14-kX basal spacing.

Slaughter and Milne(33) have given the X-Ray diffraction patterns of these modified bentonites to chlorites except that of ferric chlorite. The basal spacings of the complexes prepared by Slaughter and Milne ranging from 14.6 - 14.8 A are larger than the normal 14.2 A of naturally occuring chlorites. This results from the necessity of accomodating the original exchange cations of the montmorillonite used.

Naturally occuring chlorites rich in iron give weak first and third order and strong second and fourth order peaks.

Stain tests for clay minerals:

Several colour reactions of organic compounds and clays are known and are used for identification purposes, Hasegawa (159). The acid base reactions are generally performed after acid treatment of the clay,which may itself destroy the structure of the clay mineral. The oxidation reduction reactions obtained with benzidine staining tests,yield purple blue colour with certain montmorillonites,but no colourations are observed with other clays. The benzidine reaction is,therefore, used to identify montmorillonites in an unknown clay mixture.

Little study has been devoted to an analysis of the mechanism of oxidation of the organic compounds in presence of clays. It has been assumed that ferric ions in the octahedral sheets are responsible for oxidation of the organic compound. If so, the reaction would probably take place at the broken edges rather than on the layer surfaces of the clay. However, the possibility of oxidation by oxygen adsorbed on the layer surfaces, somehow catalyzed by the clay, cannot be excluded.

The general applicability of staining tests for the identification of the clay minerals is restricted, because of the development of characteristic colour, reactions can be inhibited, augmented or masked by several common ingredients of clay materials other than the clay minerals, Page(160). Manganese dioxide may cause the oxidation reaction with benzidine, and ferrous iron or other reducing agents may prevent the colour formation reaction from taking place. Iron and magnesium rich montmorillonites might not appear to react with the staining solutions. Also the strong original colour of a sample particularly rich in iron might tend to mask the colour change, which would result from the adsorption of the staining reagent.

Inspite of all these obstacles, a compensatory test has been described by Mielenz et al.(161) and appears to give satisfactory results. The test of Hendricks and Alexander (162) is also used for the identification of the montmorillonite type of clay minerals.

Infrared spectroscopic studies:

Keller and Pickett (105-106) and Kerr and collaborators (107) are the pioneer workers, as regards the application of infrared spectroscopy to clay mineralogy. Buswell and Dudenbostel (163) have shown that the absorption band at 2.75 microns is due to unbounded OH and that bonded OH caused absorption at 2.7-3.2 microns and again at 6.15 to 7.55 microns. The absorption at about 6.1 microns shown by some of the clay minerals is believed due to adsorbed water and the absorption at about 9.0 microns is believed due to the Si-O linkages. The octahedral alumina sheet is probably responsible for the absorption at about 10.0 microns. The causes of many of the absorption bands shown by the clay minerals are not yet understood. For example, the causes of variations in the spectra within the montmorillonite group cannot yet be related to variations of composition or structure.

According to Adler(164) the minerals of the montmorillonite group are related structurally to talc and pyrophillite. Absorption curves obtained from high alumina montmorillonite films prepared from suspensions show some resemblance to those of the kaolin minerals. Magnesium montmorillonite shows a single band at approximately 1015cm^{-1}. Spectra of nontronite, a ferrian montmorillonite,shows absorption bands at approximately 1030, 853 and 820 cm^{-1}. The band at 920 cm^{-1} is associated with the vibrations of the gibbsite layer. 820 cm^{-1} band is attributed to the O-Fe-OH layer. Band at 1120 cm^{-1} is assigned to the O-Al-OH layer.

Absorption bands observed at 3600 cm^{-1} in case of muscovites and chlorites are probably due to lattice OH. Bands were also observed at 2045 cm^{-1} and 1790 cm^{-1}. Numerous small bands are present between 2200and 3200 cm^{-1}.

Since the lattice water of the clays is tied up within the metal oxide-hydroxide layers as OH groups, the degree to which this water is bound may be discernible from an examination of the infrared spectra of these hydroxides. Differences may exist among the various clay minerals with respect to the degree and the type of OH bonding. The OH groups in minerals may exist independently of one another or they may be attracted to each other as a result of the polarizing influences exerted by the cations to which they are bound.

Absorption curve of brucite from Texas, was characterized by the absence of any absorption features. Gibbsite shows a major band at 1022 cm^{-1} and a less intense at 970 cm^{-1}. Absorption is most intense for Boehmite at approximately 1085 cm^{-1}.

EXPERIMENTAL

Preparation of chlorites:

Six gms. of B.D.H. Bentonite were shaken with 100 ml. of water on the magnetic stirrer and treated as follows: a 100 ml. of 2N metal chloride solution(Mg^{++}, Ni^{++}, Al^{+3}, Fe^{+3}), prepared from A.R. samples,was added to 100 ml. of the clay suspension. The mixture was vigorously stirred with the help of a magnetic stirrer. To the suspension was then added, dropwise 200 ml. of 1N ammonium hydroxide solution keeping the whole mass stirred. The rate of addition was such that the whole process of neutralization took about ten to twelve hours. The material was then filtered and washed repeatedly with a 1:1 mixture of water and ethyl alcohol till the filtrate was free from the chloride and the hydroxide ions. The clay thus obtained was kept in the electric oven at 105°C for 48 hours for dehydration of the adsorbed water and again kept for three months in a dry state to afford ageing. In this way a large amount of the clay (about 500 gms.) was prepared and stocked for use. In case of Nickel chlorite preparation NaOH of the same strength in place of NH_4OH was used.

Exchangeable cations:

Total exchangeable cations were found out by the method of Bray and Willhite (150).

Ten gm. of the air-dry clay (oven dry clay complex in this case) were mixed with 500 ml. of 1N neutral ammonium acetate solution and kept stirring for six hours in a mechanical shaker. The mixture was filtered and leached with another 250 ml. neutral 1N ammonium acetate solution. The filtrate was evaporated to dryness on a water bath. The residue was taken in a china dish and gently heated for fifteen minutes over a Bunsen burner and then over the red hot electric plate for half an hour. After cooling an excess of the standard acid(HCl) was added and the solution warmed, the bottom of the dish being continuously rubbed with a police man. Then the back titration was made with the standard alkali (NaOH) using methyl red as the indicator. In a very similar manner the metal hydroxides were also subjected to this analysis and the results for the so called exchange of the hydroxides obtained by this method are also given. Calculation was made on the basis that

one litre of any normal acid $\equiv$ one gm.equivalent of any base.

or

one ml.of normal acid $\equiv$ one mgm.equivalent of base.

or

c.e.c. in m.e.q. per 100 gm. of soil

$$= \frac{\text{Quantity of the acid x normality x 100}}{\text{Wt.of the soil taken.}}$$

Exchangeable hydrogen was estimated by the third method of Parker(151).

Ten gm. of the clay were placed in a Gooch crucible and leached with 500 ml. of neutral 1N barium acetate solution having a pH of 7.0 measured against both a glass-calomel electrode assembly and the quinhydrone electrode. The leachate was then titrated with N/10 $Ba(OH)_2$ solution to a pH of 7.0 measured electrometrically first with the glass-calomel electrode and then more accurately with the quinhydrone electrode.

Polarographic estimation:

Firstly the method given by Holtzinger et al.(157) was followed.

Five gm. of the clay sample was taken in a 150 ml. conical flask, to which 50 ml. of 1N $MnCl_2$ solution was added, and kept stirring for six hours in a mechanical shaker, after which the sample was centrifuged for ten mts. at 3000 r.p.m. and the supernatant liquid decanted. This operation was repeated five more times, except that now for shaking only one hour was given. The contents of the centrifuge tubes were then washed with 75% ethanol, shaking manually, centrifuging, decanting and discarding the supernatant liquid. 50 ml. of ethanol was used in each operation. Total number$ of washings given were six. The adsorbed manganous ions were then replaced by shaking again the contents of the centrifuge tubes, now, with 50 ml. of 1N KCl for ten hours, centrifuging and decanting into a 250 ml. volumetric flask. This operation was repeated four times except that the time for shaking was, now, only one hour. Solution was diluted with 1N KCl to volume(250 ml.) and thoroughly mixed. A 20 ml. aliquot of the KCl solution containing the replaced manganous ions was transferred to the cathode cell of the polarograph and to it was added 0.1 ml. of 0.001% gelatin solution. After removal of dissolved oxygen by passage of nitrogen through the solution a polarogram was obtained. Concentration of the manganous ions in this unknown solution was then calculated from the polarogram by use of a previously drawn calibration curve.

Polarograph used was that of the Toshniwal Bros. (India). Readings were taken against a standard saturated calomel electrode at $30^{\circ} \pm 0.1^{\circ}$C . Drop time, open circuit, was 3.4 sec. and $m^{2/3} t^{1/6}$ was 2.877.

In the second method, instead of manganous chloride solution, zinc chloride solution was used, other details were th same as in the preceding experiment.

Blank experiments with the metal hydroxides were also performed which did not show any exchange reaction by this method.

Complete details of these results obtained are not given, typical curves obtained in case of only some of these clays are shown in Fig.2 a and b.

<u>Flame photometric estimation</u>:

Interference filters were available only for Na, K and Ca and so for the measurements of these exchange cations the following procedure was adopted.

Ten gm. of the clay were mixed with 500 ml. of 1N neutral ammonium acetate solution and kept stirring for six hours in a mechanical shaker. The mixture was filtered and leached with another 250 ml. neutral 1N ammonium acetate solution. The filtrate was evaporated to dryness on a water bath. The residue was taken in a china dish and gently heated for fifteen mts. over a Bunsen burner and then over the red hot electric plate for half an hour. After cooling, the residue was taken in 20 ml. of 0.2 N HCl, the solution being warmed, the bottom of the dish being continuously rubbed with a police man.

Preliminary experiments had shown that the concentrations of the interfering ions like phosphate,aluminum and iron were too small to hinder in the direct estimation of the exchange cations without the removal of these interfering ions. Experimental results obtained after removal of these interfering ions and without removal were identical and, therefore,no attempt was made to remove these interfering radicals.

Direct estimations of the exchange cations were made with the proper filter introduced and keeping the other constants like slit width, gas pressure and air pressure the same as in getting the calibration curve (Fig.1) of an equimolecular mixture of these three cations in HCl of the same strength. Standard calibration curves thus obtained were repeatedly checked from one series of determinations to another. Standard solution of the cations were prepared by dilution from a concentrated stock solution.

The acid solution obtained after digestion of ammonium acetate was filtered to remove any precipitated silica through a Gooch crucible fitted with discs of filter paper , as given by Chesnin and Johnson (166).

For determining the total exchangeable cations the weighed quantity of the clay sample was first leached as usual with normal calcium chloride solution of pH 7.0 and after thorough washing with alcohol it was again leached with neutral normal ammonium acetate solution. Rest of the procedure was the same as for determining the individual exchange cations. The quantity of calcium was then measured in the acetate extract of these samples as usual from its own calibration curve.

Blank experiments were also performed with the metal hydroxides which gave exchange values as in the previous experiment.

A calibration curve is shown in Fig.1 but other detailed results are not mentioned.

Carl Zeiss Flame Photometer Model III was used for the purpose. Petrol gas being used throughout the work.

Total exchangeable cations in m.e.q.per 100 gm.clay were calculated as-

$$\frac{\text{Concentration of } Ca^{++} \text{ ions in percent}}{100} \times \frac{\text{Quantity of the soln.}}{\text{At.Wt. of calcium}} \times \frac{1000 \times 100}{\text{Wt. of clay taken}}.$$

Chemical analysis:

It was carried out in accordance with the details given by Jackson(82) and Wright(81).

Stain tests for clay minerals:

A pulverized portion of all the clay minerals (transformed) including bentonite was treated separately with benzidine solution. A purple blue colouration was observed in case of bentonite only and with others no colour was developed. In a similar fashion the acid treated clays, washed free of chloride ions, were treated with malachite green in nitrobenzene. A yellow colour developed in case of bentonite only. No other (transformed) clay gave any colour.

Similarly the metal hydroxides were also treated with benzidine in which case again no colour was developed. Probably, the absence of any colour in case of $Fe(OH)_3$ is due to the masking effect.

To make double sure the results, mixtures of bentonite with metal hydroxides in an approximately equal ratio as in the respective chlorites were again treated with benzidine and the purple blue colour was observed in each case. Even in case of ferric hydroxide-bentonite mixture the blue shade could be observed; all this confirms the complete conversion of bentonite structure.

Infrared spectroscopic analysis:

I.R.Spectra were taken on a Perkin Elmer Spectrophotometer No.021. Results are shown in Figs.8 a,b,and c.

Dehydration curves:

A known weight of the clay sample was taken in a platinum crucible whose weight was found out to remain constant by heating upto 1000°C in an electrically controlled muffle furnace to an accuracy of ± 5°C. The sample was heated in the furnace to a given temperature, cooled inside the furnace and then the desiccator, weighed, and reheated to the same temperature and cooled and weighed till the weight was constant and did not decrease by further heating at that temperature. The whole operation took about six hours. It was then heated to a higher temperature and held at that temperature until no loss in weight took place. This process was repeated until the maximum temperature of the furnace i.e., 1000°C was reached. The loss in weight was plotted against the temperature of heating. In exactly a similar manner the dehydration curves for the metal hydroxides taken were also drawn. Curves for the pure clay sample were obtained by subtracting the metal hydroxide curves from the montmorillonite-metal hydroxide complex curves, assuming the complete conversion of montmorillonite to chlorite as proved by other physico-chemical studies. Results are shown in Figs. 3,4 and 5.

Differential thermal analysis:

Leeds and Northrup semi automatic D.T.A. apparatus was used for the work described, in conjunction with a sensitive Scalamp galvanometer. Rate of heating was controlled by an automatic arrangement and was 10°C per minute. The sample was a rectangular block and the inert material used for reference was α-alumina. A Pt-Pt-Rh thermocouple was used. The sample holder was of the Grimshaw type, (167). Samples were passed through 200 mesh British Standard Sieve. Results are shown in Figs. 6 and 7.

X-Ray diffraction analysis:

The X-Ray diffraction patterns were obtained with the help of a Philips 1051 PW Diffractometer using Phlips 1010 PW X-Ray generator and a scintillator counter instead of the G.M. Tube. Samples were ground to pass 350(B.S.S.) mesh. Copper target with nickel filter was used for bentonite, magnesium chlorite and aluminum chlorite whereas iron target with manganese filter was used in case of ferric chlorite and nickel chlorite. Work was done at 26 KV and 10 m.a..

Scan speed and chart speed were 2° per mt.and 800 m./h.in every case. Other details for the individual cases are given in the table below.

Sample.	2 θ range. (degree)	Scale factor.	Rate meter.	Diagnol slit. (degree)	Receiving slit. (degree)
Bentonite	4 - 18	64,64	2,1	1	1/2
	18 - 65	32,32	"	"	2
$Mg(OH)_2$	16 - 17	"	"	"	1
" Heated	30 - 80	"	"	"	"
Mg-chlorite	3 - 16	"	"	1/2	1/2
	16 - 70	"	"	1	1
" Heated	3 - 16	"	"	1/2	1/2
	16 - 80	"	"	1	1
$Al(OH)_3$	16 - 60	"	"	"	"
" Heated	16 - 70	"	"	"	"
Al-chlorite	3 - 15	"	"	1/2	1/2
	15 -60	"	"	1	1
" Heated	3 - 16	"	"	1/2	1/2
	16 - 70	"	"	1	1
$Fe(OH)_3$	16 - 90	32,8	4,1	"	0.2
" Heated	16 - 90	"	"	"	"
Fe-chlorite	3 - 16	"	"	1/2	"
	16 - 90	"	"	1	"
" Heated	3 - 16	"	"	1/2	"
	16 - 90	"	"	1	"
$Ni(OH)_2$	20 - 90	"	"	"	"
" Heated	40 - 90	"	"	"	"
Ni-chlorite	3 - 16	"	"	1/2	"
	16 - 90	"	"	1	"
" Heated	3 - 16	"	"	1/2	"
	16 - 90	"	"	1	"

Results are shown in Figs.9-12.

FLAME PHOTOMETRIC ANALYSIS OF Ca, Na & K IN HCL SOLUTION

(Calibration curves)

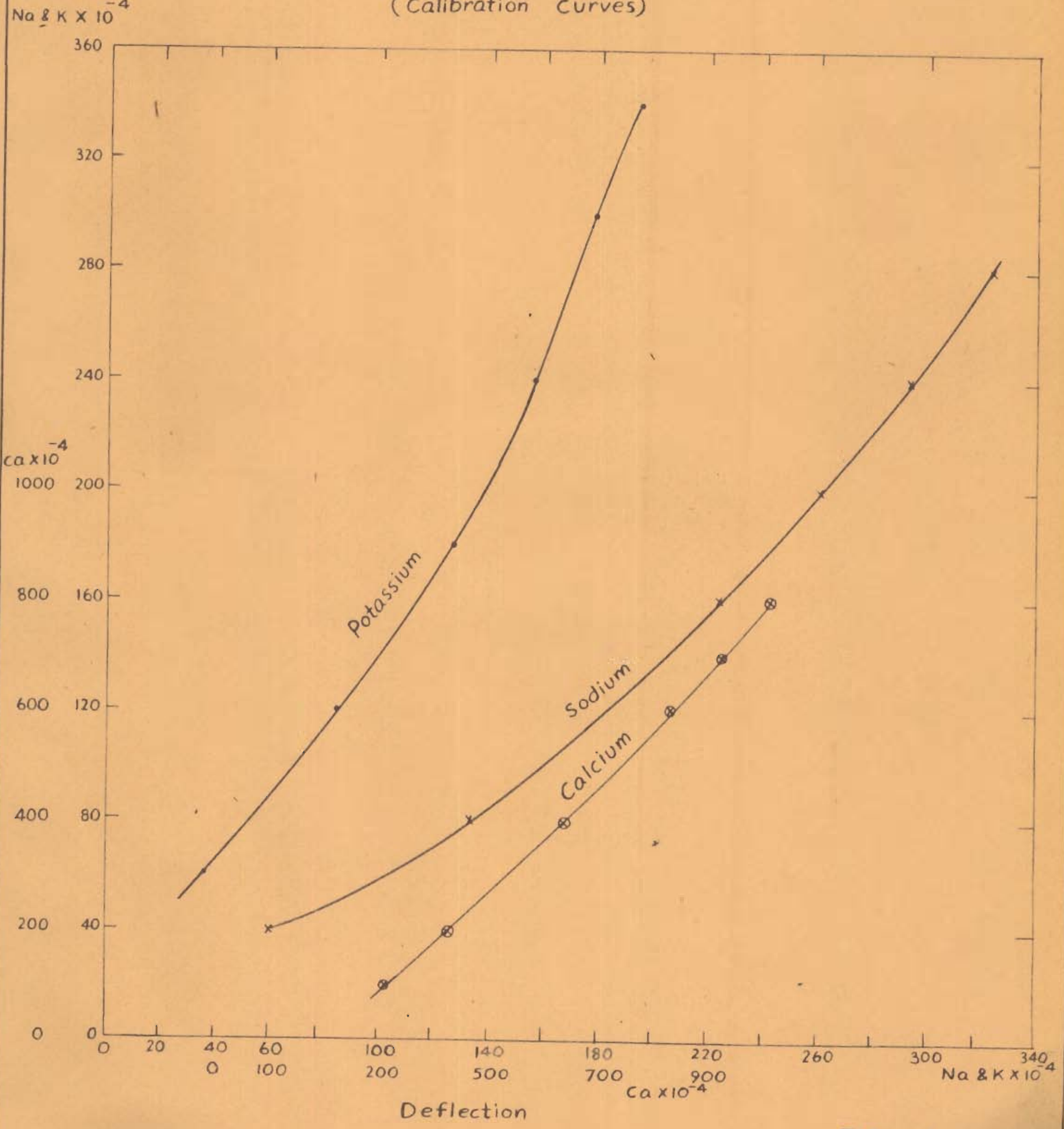


FIG. 1

POLAROGRAMS OBTAINED WITH
(i) FERRIC & (ii) ALUMINIUM CHLORITES
WITH MANGANOUS ION REPLACEMENT

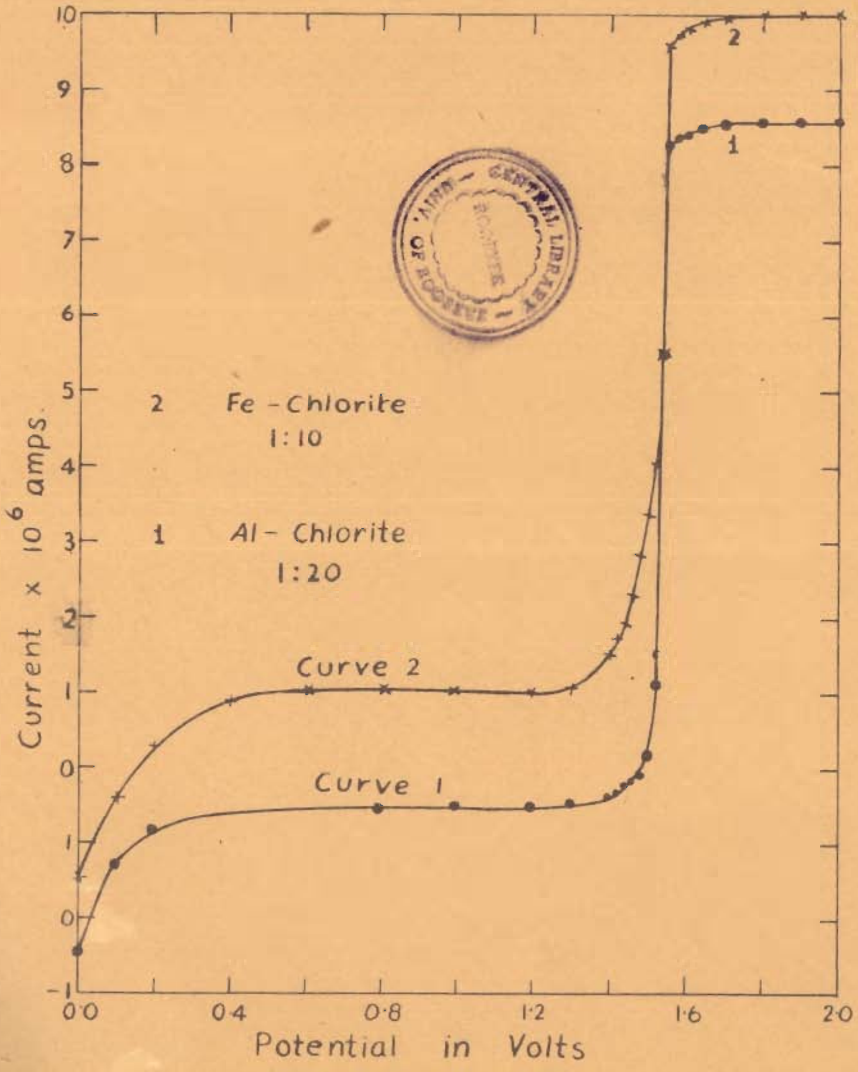


FIG · 2 (a)

POLAROGRAMS OBTAINED WITH
(i) BENTONITE & (ii) Ni-CHLORITE
WITH ZINC ION REPLACEMENT

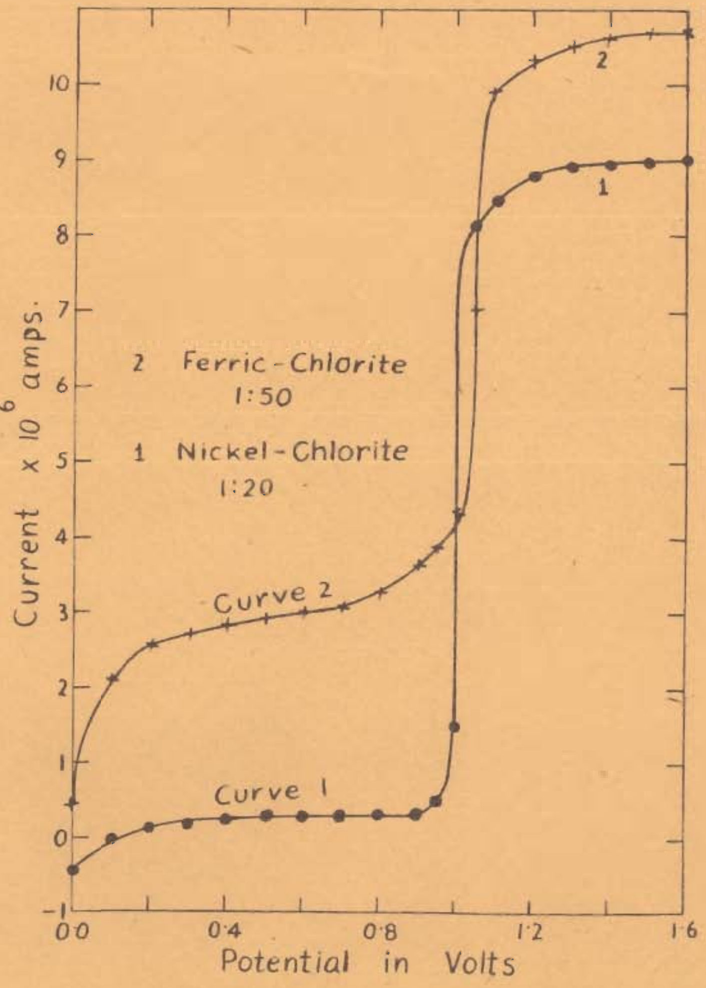


FIG 2(b)

RESULTS

TABLE No. 1

Weights of the bentonite-metal hydroxide complexes obtained from six gm. of B.D.H.bentonite.

1. Al-chlorite + Al $(OH)_3$ = 16.0 gm.
2. Fe-chlorite + Fe $(OH)_3$ = 25.0 gm.
3. Mg-chlorite + Mg $(OH)_2$ = 17.0 gm.
4. Ni-chlorite + Ni $(OH)_2$ = 24.0 gm.

TABLE No.1(a).

Assuming complete conversion of bentonite to respective chlorite,as proved by the various physico-chemical methods, the ratios of the chlorite to free metal hydroxide present in bentonite metal hydroxide complexes.

1. Al-chlorite : $Al(OH)_3$ = 3:5
2. Fe-chlorite : $Fe(OH)_3$ = 6:19
3. Mg-chlorite : $Mg(OH)_3$ = 6:11
4. Ni-chlorite : $Ni(OH)_2$ = 1:3

TABLE No.2

Total exchangeable cations in the bentonite-metal hydroxide complexes by the ammonium acetate method.

Weight of the mixture taken = 10.o gm.

Quantity of N/10 HCl added = 20.0 ml.

Complex	Amt.of N/10 NaOH used.ml.	Amt.of N/10 HCl left unused. ml.	Total exchangeable cation in m.e.q. per 100 gm.mixture.
Bentonite-$Al(OH)_3$	4.5	15.5	15.5
Bentonite-$Fe(OH)_3$	12.0	8.0	8.0
Bentonite-$Mg(OH)_2$	11.5	8.5	8.5
Bentonite-$Ni-(OH)_2$	15.2	4.8	4.8
* Bentonite	10.91	9.09	90.9

* Weight of bentonite taken is only one gm.

TABLE No.2(a).

Exchange values with the metal hydroxides by the ammonium acetate leaching method.

Weight of the hydroxide taken. = 10.0 gm.

Quantity of HCl N/10 added in each case. = 10.0 ml.

Hydroxide.	Amt.of N/10 NaOH used. ml.	Amt.of N/10 HCl left unused.ml.	Exchange values in m.e.q.per 100 gm. of the hydroxide.
$Al(OH)_3$	4.4	5.6	5.6
$Fe(OH)_3$	7.5	2.5	2.5
$Mg(OH)_2$	6.3	3.7	3.7
$Ni(OH)_2$	7.6	2.4	2.4

TABLE No.2(b).

Exchangeable hydrogen:

No change in pH of the barium acetate leachate was found and hence there is no exchangeable hydrogen in any of the transformed clays.

Weight of bentonite taken. = 1.0 gm.

Amount of barium acetate extract. = 250 ml.

Amount of barium hydroxide required to make the pH 7.0. = 1.52 ml. N/10

Exchange hydrogen in bentonite. = 15.2 m.e.q. per 100 gm. clay.

TABLE No.3.

Comparative data on exchangeable cations determined by different methods,(derived for the chlorites taking the ratio of chlorite to metal hydroxide as given in Table 1 a).

Method.	Aluminum chlorite.	Ferric chlorite.	Magnesium chlorite.	Nickel chlorite.	Bentonite.
Amm.Acetate replacement.	32.0	25.4	17.3	12.0	90.9
Flame photometry.	32.8	26.2	16.6	11.4	88.75
Polargography a.Mn^{+2}	32.3	25.2	17.6	12.0	87.5
b. Zn^{+2}	28.8	22.1	14.5	11.2	83.1

TABLE No.4.

Chemical analysis.

Contents percent.	Aluminium chlorite.	Ferric chlorite.	Magnesium chlorite.	Nickel chlorite.	Bentonite.
Nitrogen.	0.0873	0.0324	0.0364	0.0672	0.1520
Carbon.	0.6624	0.0245	0.2760	0.5100	0.1228
Nitrate nitrogen.	0.0477	0.0162	0.0182	0.0336	0.0930
Ammonia nitrogen.	0.0034	0.0012	0.0014	0.0026	0.0052
$Si\ O_2$	10.12	10.65	13.59	14.08	41.52
Al_2O_3	56.46	3.89	6.84	3.62	18.37
Fe_2O_3	4.83	60.78	5.55	3.05	14.21
MgO	0.50	0.60	47.07	0.54	1.46
CaO	0.20	0.15	0.06	0.03	1.25
MnO	0.005	0.01	0.008	0.006	0.02
NiO	-	-	-	63.10	-
Water	27.2	22.9	26.1	14.5	21.3
Total	100.1158	99.0543	99.5500	99.5394	98.5530

DEHYDRATION CURVES OF BENTONITE AND ITS COMPLEXES WITH METAL HYDROXIDE

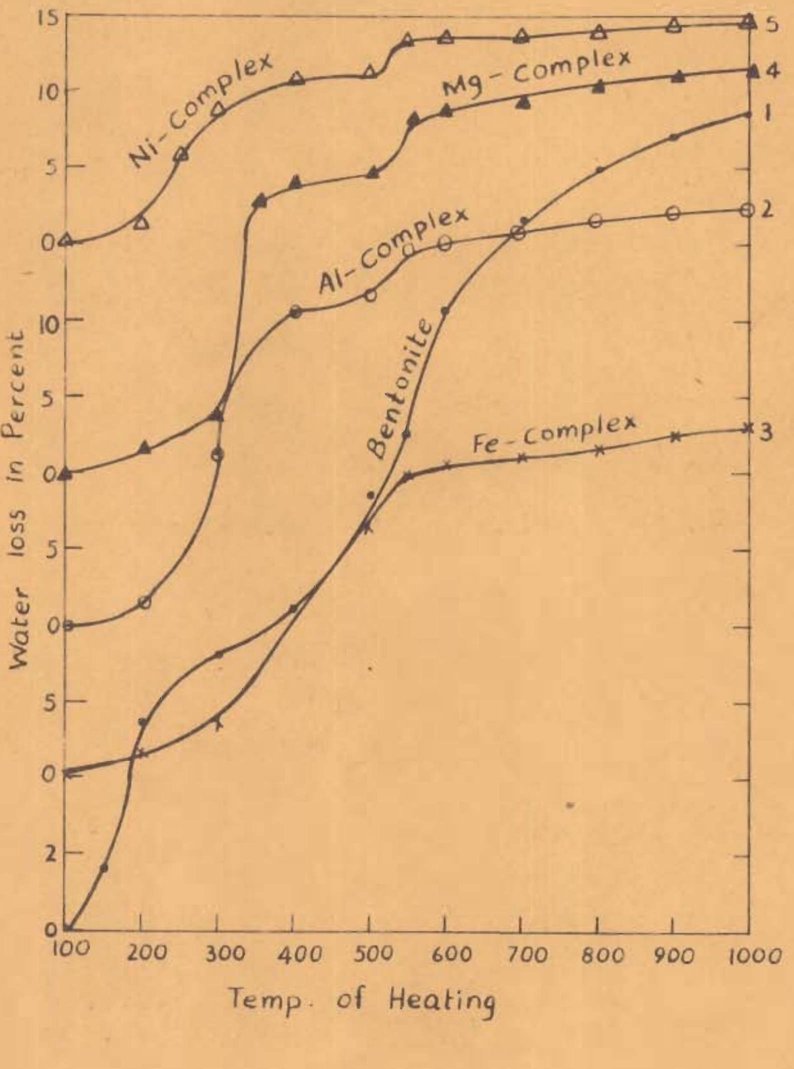


FIG. 3

TABLE No. 5.

Dehydration data for montmorillonite-metal hydroxide complexes dried at 105°C.

	Magnesium chlorite.		Nickel chlorite.		Aluminum chlorite.		Ferric chlorite.		Bentonite.	
Temp. of heating °C	Wt. of complex gm.	Water loss %	Wt. of complex gm.	Water loss %	Wt. of complex gm.	Water loss %	Wt. of complex gm.	Water loss %	Wt. of complex gm.	Water loss %
105	2.5350	-	3.2371	-	2.8571	-	3.0592	-	3.2571	-
150	-	-	-	-	-	-	-	-	3.2049	1.62
200	2.4923	1.7	3.1989	1.2	2.8100	1.4	3.0070	1.7	3.1808	5.40
250	-	-	3.0491	5.8	-	-	-	-	-	-
300	2.4340	4.00	2.9479	8.9	2.5311	11.2	2.9521	3.5	3.0222	7.19
350	2.0813	17.90	-	-	-	-	-	-	-	-
400	2.0582	19.00	2.8910	10.7	2.2580	20.6	2.7099	11.4	2.9493	8.41
500	2.0351	19.70	2.8772	11.1	2.2199	21.9	2.5478	16.7	2.8864	11.38
550	1.9490	23.10	2.8088	13.2	2.1488	24.6	2.4533	19.8	2.8338	12.97
600	1.9339	23.70	2.8031	13.4	2.1382	25.0	2.4369	20.4	2.7260	16.33
700	1.9192	24.3	2.7945	13.7	2.1170	25.7	2.4161	21.0	2.6511	18.62
800	1.8929	25.3	2.7907	13.8	2.0955	26.5	2.4042	21.5	2.6077	19.96
900	1.8811	25.8	2.7744	14.3	2.0810	27.0	2.3760	22.4	2.5796	20.78
1000	1.8740	26.1	2.7680	14.5	2.0750	27.2	2.2899	22.9	2.5645	21.30
	Fig.3, curve 4.		Fig.3, curve 5.		Fig.3, curve 2.		Fig.3, curve 3.		Fig.3, curve 1.	

DEHYDRATION CURVES OF METAL HYDROXIDES

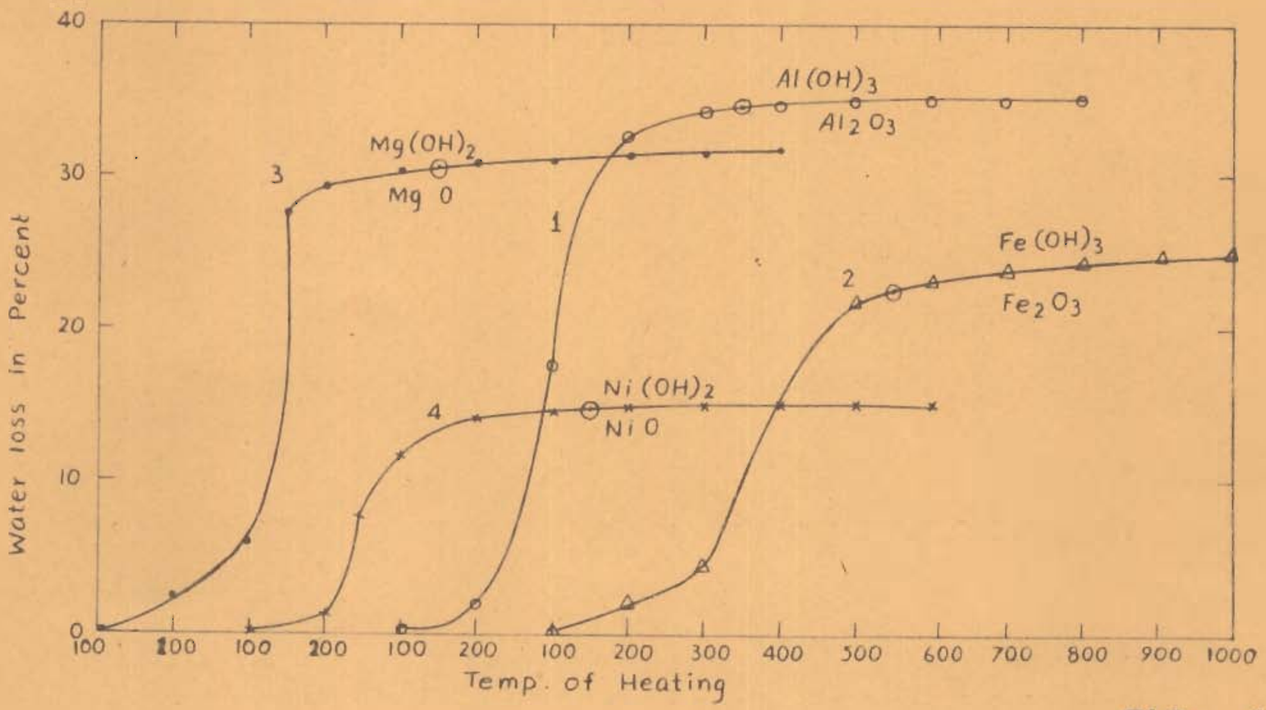


FIG · 4

DEHYDRATION CURVES (DERIVED) FOR CHLORITES

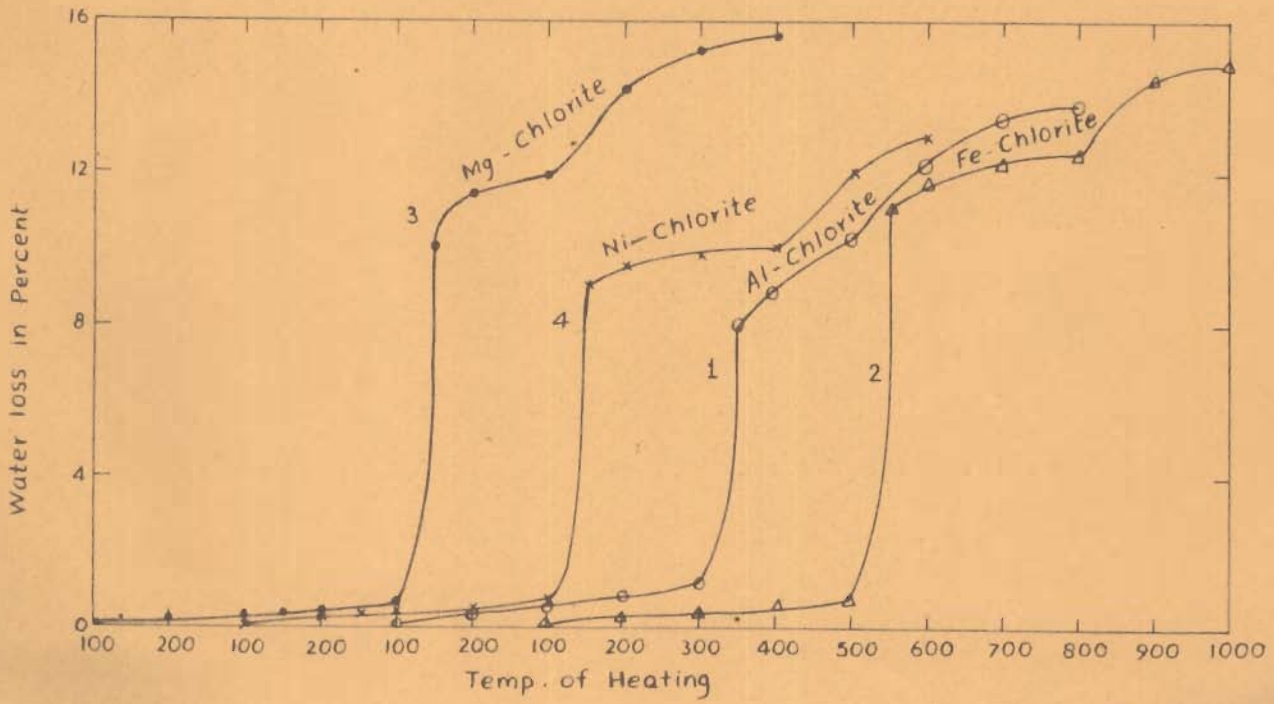


FIG · 5

TABLE No.6

Dehydration data for the metal hydroxides dried at 105 °C.

Temp. of heating °C.	Magnesium hydroxide.		Nickel hydroxide.		Aluminum hydroxide.		Ferric hydroxide.	
	Wt. of hydroxide gm.	Water loss %	Wt. of hydroxide gm.	Water loss %	Wt. of hydroxide gm.	Water loss %	Wt. of hydroxide gm.	Water loss %
105	2.7691	-	2.3270	-	3.5792	-	3.7995	-
200	2.7000	2.5	2.2921	1.5	3.5039	2.1	3.7191	2.1
250	-	-	2.1500	7.6	-	-	-	-
300	2.6021	6.0	2.0553	11.7	2.9488	17.6	3.6282	4.5
350	2.0073	27.5	-	-	-	-	-	-
400	1.9605	29.2	2.0009	14.0	2.4135	32.6	3.2362	14.8
500	1.9359	30.1	1.9905	14.5	2.3520	34.3	2.9753	21.7
550	1.9302	30.3	1.9876	14.6	2.3399	34.5	2.9439	22.5
600	1.9239	30.5	1.9859	14.7	2.3370	34.7	2.9174	23.2
700	1.9108	31.0	1.9781	15.0	2.3273	35.0	2.8948	23.8
800	1.9019	31.3	1.9779	15.0	2.3234	35.1	2.8006	24.4
900	1.8968	31.5	1.9775	15.0	2.3230	35.1	2.7873	24.9
1000	1.8881	31.8	1.9773	15.0	2.3161	35.3	2.7811	25.1
	Fig.4, curve 3.		Fig.4, curve 4.		Fig.4, curve 1.		Fig.4, curve 2.	

TABLE No.7

Dehydration data for the various chlorites, obtained by subtracting the results of metal hydroxides from those of bentonite-metal hydroxide complexes.
Ratios taken from Table No.1(a).

Temp. of heating. °C	Loss of water percent.			
	Mg. chlorite	Ni. chlorite	Al. chlorite	Fe. chlorite.
105	-	-	-	-
200	0.2	0.2	0.3	0.3
250	-	0.4	-	-
300	0.3	0.5	0.6	0.5
350	0.36	-	-	-
400	0.40	0.6	0.9	0.6
500	0.70	0.9	1.2	0.8
550	10.00	9.1	8.1	11.1
600	11.4	9.5	8.9	11.7
700	11.9	9.8	10.3	12.2
800	14.2	10.0	12.2	12.5
900	15.2	12.1	13.5	14.4
1000	15.6	13.0	13.8	14.6
	Fig.5, curve 3.	Fig.5, curve 4.	Fig.5, curve 1.	Fig.5, curve 2

DIFFERENTIAL THERMAL ANALYSIS CURVES OF BENTONITE & ITS COMPLEXES WITH METAL HYDROXIDES

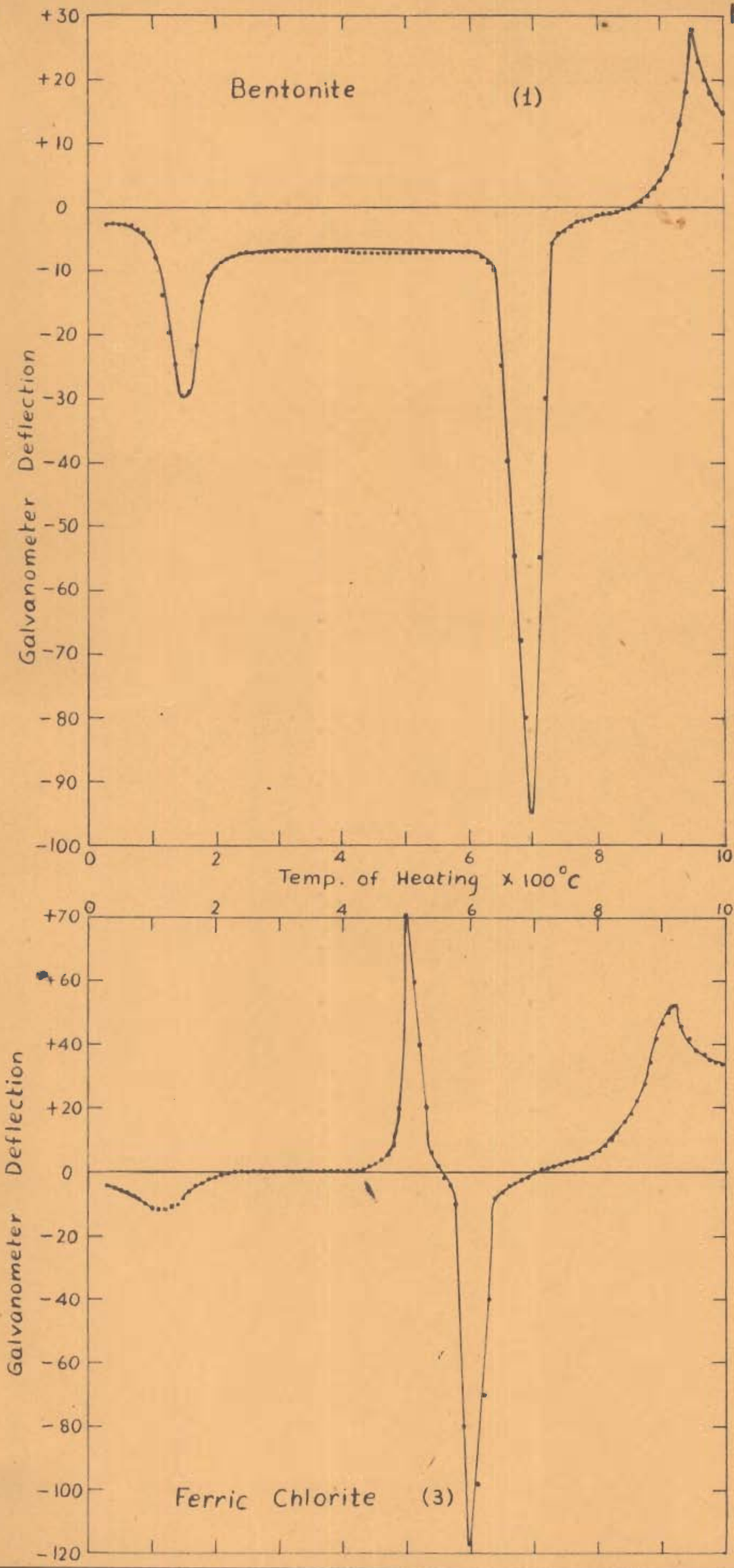


FIG. 6

DIFFERENTIAL THERMAL ANALYSIS CURVES. OF BENTONITE & ITS COMPLEXES WITH METAL HYDROXIDES

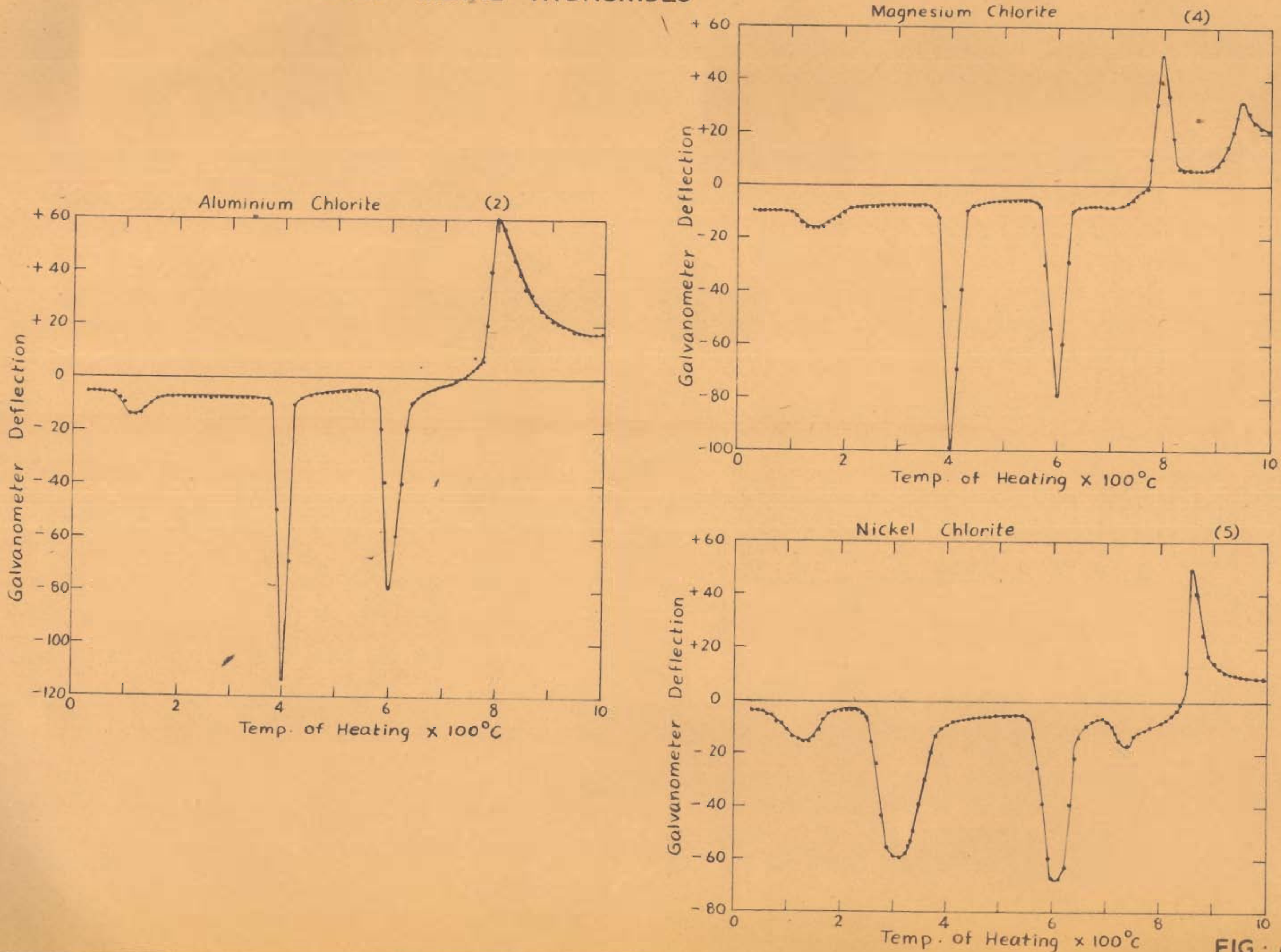
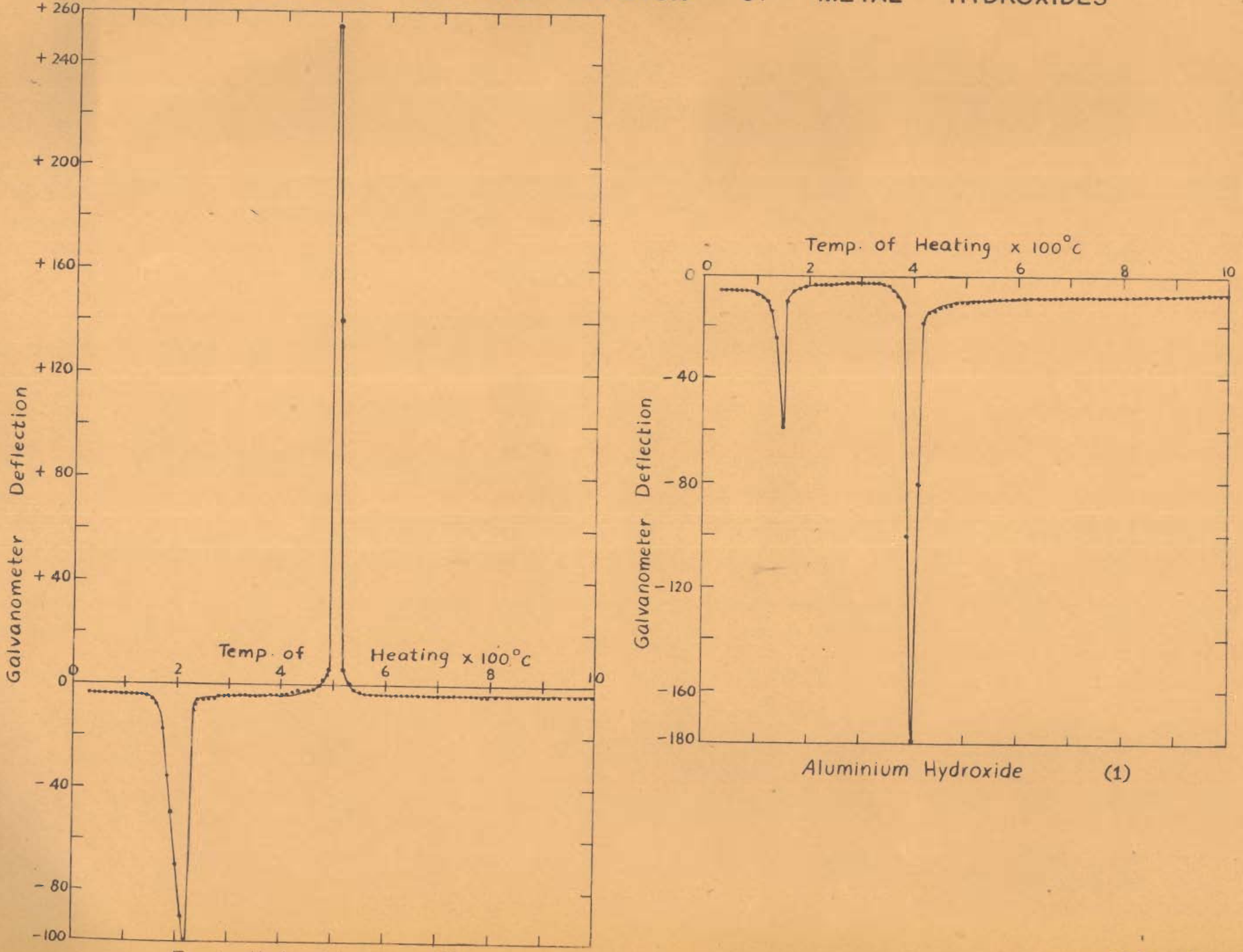


FIG · 6

DIFFERENTIAL THERMAL ANALYSIS OF METAL HYDROXIDES

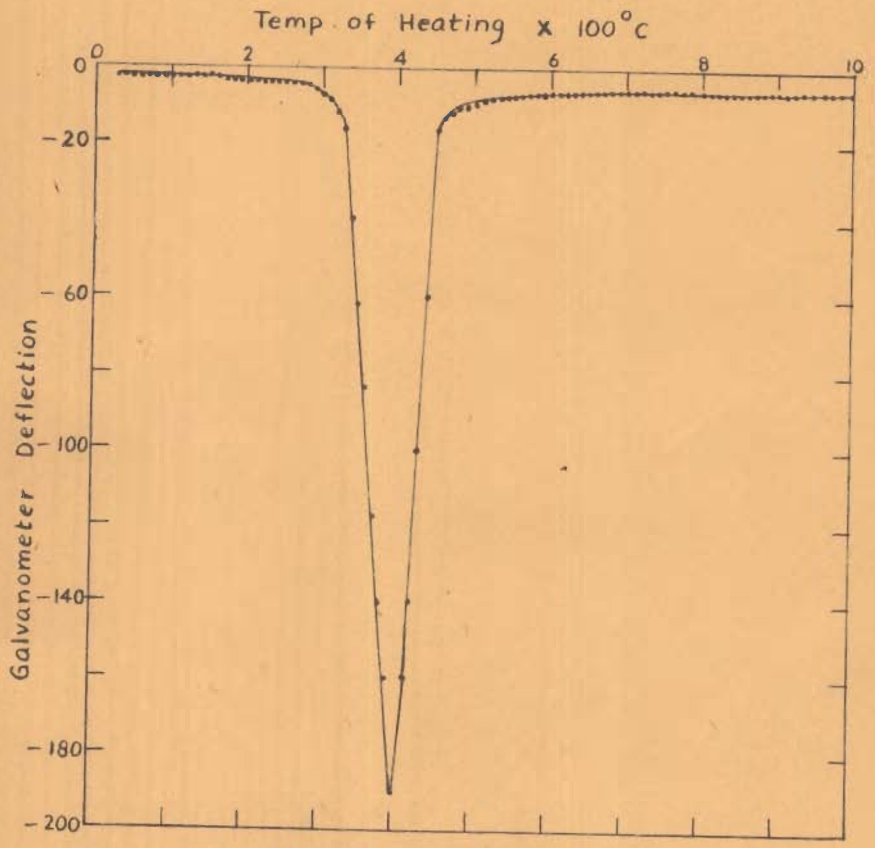


Ferric Hydroxide (2)

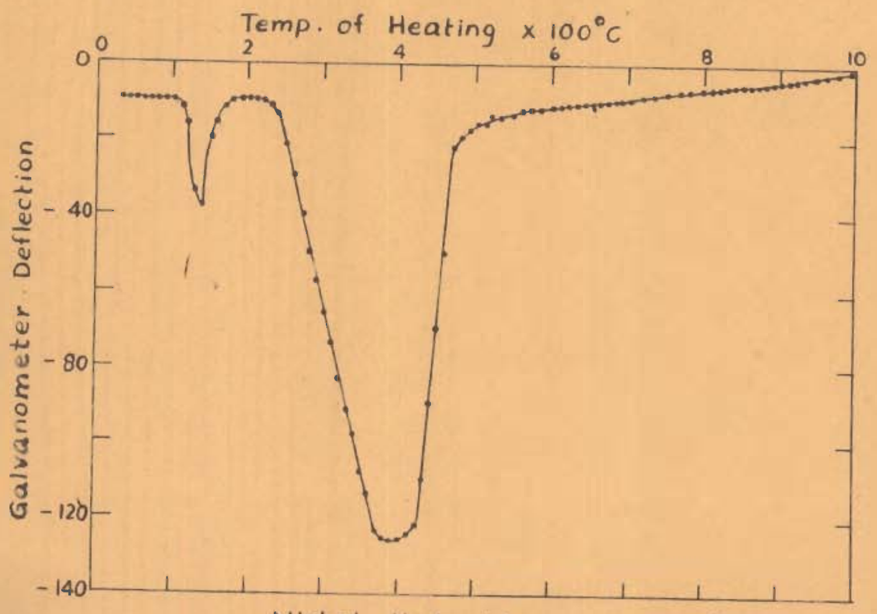
Aluminium Hydroxide (1)

FIG. 7

DIFFERENTIAL THERMAL ANALYSIS OF METAL HYDROXIDES



Magnesium Hydroxide (3)



Nickel Hydroxide (4)

FIG. 7

TABLE No. 8.

Differential thermal data.

Peak temp. °C and relative shapes and sizes.

	Reaction.		
Substance.	Endothermic.	Exothermic.	
Magnesium hydroxide.	400,v.l. sharp.	-	Fig.7,curve 3.
Nickel hydroxide.	i 130,s. sharp. ii 390,l. broad.	- -	Fig.7,curve 4.
Ferric hydroxide.	220,l. sharp.	500,v.l. v.sharp.	Fig.7,curve 2.
Aluminum hydroxide.	i 150,l. sharp. ii 400,v.l. v.sharp.	- -	Fig.7,curve 1.
Bentonite.	i 150,l. broad. ii 700,v.l. sharp.	950,l. sharp. -	Fig.6,curve 1.
Magnesium chlorite complex.	i 150,v.s. broad. ii 400,l. sharp. iii 600,l. sharp.	i 800,l. sharp. ii 950,s. broad.	Fig.6,curve 4.
Nickel chlorite complex.	i 150,s. broad. ii 310,l. diffuse. iii 600,l. broad. iv 730,v.s. broad.	860,l. sharp.	Fig.6,curve 5.
Ferric chlorite complex.	i 120,s. broad. ii 600,v.l. v.sharp.	i 500,l. v.sharp. ii 920,l. broad.	Fig.6,curve 2
Aluminum chlorite complex.	i 120,s. broad. ii 400,v.l.sharp. iii 600,l.sharp.	800,l. broad.	Fig.6,curve 1.

TABLE No.9.

Infrared absorption data for the clay minerals.

Clay sample	Position of band centres, cm.$^{-1}$	
Bentonite.	3700,3450,3180,1650,1040,670.	Fig. 8 a, curve 1.
Mg-chlorite complex.	3780,3450,3200,1040,970 ,920, 890,670.	Fig. 8 b, curve 1.
Ni-chlorite complex.	3700,3450,3200,1660,1025,920, 800,670.	Fig. 8 b, curve 2.
Al-chlorite complex.	3550,1650,1060,1000,920 , 800.	Fig. 8 c, curve 1.
Fe-chlorite complex.	3700,3520,3200,1150,1040,970,940,920, 890, 850,790,670.	Fig. 8 c, curve 2.

TABLE No.10

X-Ray diffraction data.

Bentonite		Mg(OH)$_2$		Mg-chlorite complex. unheated.		Mg(OH)$_2$ heated, 600°C.		Mg-chlorite complex. Heated 600°C.		Al(OH)$_3$	
d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I
11.47	100	4.76	80	14.71	100	2.43	30	14.71	55	4.71	100
5.82	20	2.72	10	7.43	60	2.10	100	7.43	15	4.37	55
4.48	60	2.36	100	4.95	80	1.48	55	4.95	15	3.20	35
3.22	15	1.79	35	4.76	75	1.27	10	3.65	10	2.21	65
2.92	15	1.57	40	3.65	60	1.21	15	2.96	5	1.72	30
2.54	70	1.49	25	2.96	30	(4 - 0829)		2.43	10	(12-457)	
2.48	35	1.37	20	2.72	20	MgO		2.10	100	Bayerite.	
2.23	20	(7-239)		2.36	80			1.48	35	Fig.9,	
1.69	40	Brucite.		1.79	30	Fig.11,		1.27	5	curve 3.	
1.49	65	Fig.11,		1.57	20	curve 4.		1.21	10		
(3-0019)		curve 2.		1.49	10			-	-	-	
				1.37	30						
Fig.9, curve 1.				Fig.11, curve 1.				Fig.11, curve 3.			

TABLE No.10 (Continued from page 58).

Al-chlorite complex.Unheated. d(A)	I	$Al(OH)_3$ Heated 600°C d(A)	I	Al-chlorite complex. Heated 600°C d(A)	I	$Ni(OH)_2$ d(A)	I	Ni-chlorite complex.Unheated d(A)	I	$Ni(OH)_2$ Heated 600°C d(A)	I
14.71	100	4.54	30	14.71	100	4.61	65B	14.6	45	2.41	90
7.30	20	2.78	30	7.30	10	2.70	100	7.32	85	2.08	100 B
4.81	60	2.39	55	4.81	30	2.33	60 B	5.00	55	1.47	40
4.71	80	2.28	40	4.54	15	1.75	10	4.61	45 B	(Bunsenite)	
4.37	45	1.97	100	3.63	10	1.56	60	3.60	25	NiO	
3.63	25	1.52	35	2.90	10	1.48	40	2.70	100	(4-0835)	
3.20	25	1.39	90	2.78	15	(β-$Ni(OH)_2$)		2.33	40 B		
2.90	20	(γ-Al_2O_3)		2.39	25	(1-1047)		1.75	10 B		
2.21	55	(3-0914)		2.28	15			1.56	40		
1.72	25			1.97	40			1.48	30		
- -	-			1.52	10			- -	-		
				1.39	40						
Fig.9,curve 2.		Fig.9,curve 5.		Fig.9,curve 4.		Fig.12,curve 2.		Fig.12,curve 1.		Fig.12,curve 4.	

(Contd...)

T A B L E No.10 (Continued from Page 59)

Ni-chlorite complex. Heated 600°C		Fe-chlorite complex. Unheated		$Fe(OH)_3$ Heated 600 °C		Fe-chlorite complex. Heated 600°C	
d(A)	I	d(A)	I	d(A)	I	d(A)	I
14.6	65	15.85	100 B	3.68	45	15.85	65
7.32	20	7.32	65	2.69	100	7.32	25
5.00	20 B	5.00	65	2.51	55	5.00	15 B
2.41	60	3.15	100 B	2.20	15	3.68	35
2.08	100	- -	-	2.08	15	3.15	15
1.47	55			1.83	25	2.69	100
- -	-			1.69	45	2.51	60
				1.59	55	2.20	20
				1.48	20	2.08	25
				1.45	25	1.83	25
				(α-Fe_2O_3) (6-0502)		1.69	55
						1.59	40
						1.48	20
						1.45	25
						- -	-
Fig.12, curve 3.		Fig.10, curve 1.		Fig.10, curve 2.		Fig.10, curve 3.	

DISCUSSION

Chemical analysis data:

These observations are in conformity with those of Hendricks (168) and Oades and Townsend(169), for the greater feasibility of the binding of organic matter with the iron of the clays, than with aluminum. The observed decrease in the quantity of the exchangeable cations of the iron clay as compared to the aluminum clay also supports the above view point.

Aluminum clay$ also differsfrom other clays in possessing the maximum quantities of exchangeable cations. This particular behaviour is due to the fact that Al^{+3} ions are not likely to displace the exchangeable cations of the original bentonite so easily as the other bivalent metal ions do.

Total exchangeable cations and chemical analysis:

The c.e.c.data obtained by the analytical method (ammonium acetate leaching) are higher than the corresponding one obtained by the polarographic method. It is, however, interesting to find that the c.e.c.values determined by the analytical method resemble closely with the results of the latter method only when due allowance is made for the values obtained for the metal hydroxides set free from these transformed clays on leaching with ammonium acetate.

It is, therefore, evident that the polarographic method, besides being less tedious and time consuming gives satisfactory results for total exchange capacity in the case of these modified clays. This method,should,therefore, invariably,be used for an accurate determination of c.e.c. of such transformed clays, and is also useful in the case of naturally occuring clay minerals. The flame photometric method has the extra advantage,over the polarographic method, in a quick and successful estimation of the individual exchange cations like sodium,potassium,magnesium and calcium. The polarographic method fails here as these cations reduce at a very high negative potential of d.m.e. and also the non-availability of a suitable supporting electrolyte. The results of flame photometric analysis for the individual exchange cations were in conformity with the data obtained by the chemical analysis method.

A closer scrutiny of the polarographic data would reveal that the data obtained by Zn^{++} ion replacement method gives lower values of c.e.c. than those obtained by the Mn^{++} ion replacement technique. This may be due to the following reasons,(a) relative dissociability of Zn^{++} and Mn^{++} ions in view of the different bonding energies of the exchange sites for these cations,(b) smaller replacing power of KCl for Zn^{++} ions in comparison to Mn^{++} ions due to its larger ionic radius.

Special considration arise in exchanges by cations which tend to form hydroxy salts, or which associate in solution. Bower and Truog (83) have shown that clays of the montmorillonite group retain more quantities of zinc,than their inherent exchange capacities. As shown by Jenny and Elgabaly (170) zinc can be held in three different forms by montmorillonites viz., Zn^{++}, $Zn(OH)^{+}$ and $ZnCl^{+}$. It may also enter in the form of "fixed" zinc in the central octahedral layers of these clays, Elgabaly and Jenny(171). Marshall (118) has also included zinc in the category of those group of ions which give abnormal values for the c.e.c. of clays. No such fixation or hydroxylation reactions have so far been reported for Mn^{++} ions. A lower value of c.e.c. using $ZnCl_2$ as the first replacing solution is, therefore, understandable.

The large decrease in c.e.c. of these transformed clays from 90 m.e.q. per 100 gm. of the clay to 12.0 (minimum) m.e.q. per 100 gm. in case of nickel chlorite and 32.0 (maximum) m.e.q. per 100 gm. of aluminum chlorite confirms the transformation of montmorillonite structure to chlorite structures. The naturally occuring chlorites are also reported to have a c.e.c. value of 10-40 m.e.q. per 100 gm. of the clay.

On comparing the results of total exchangeable cations, individual exchange cations, determined by different methods, including the method of chemical analysis, of the various bentonite-metal hydroxide complexes, it is seen that bentonite has been, undoubtedly, converted into the chlorite structure. The c.e.c. values of these clays rule out the possibility of the formation of any kaolinite for which the quoted c.e.c. values are 3-15 m.e.q. per 100 gm. of the clay, Grim(2). Absence of any exchangeable hydrogen and broken bonds also support the view point of the absence of any kaolinite.

Cation exchange capacity of the transformed clays is dependant on the following factors, (a) charge deficiency due to breakdown of the original bentonite structure,(b) lattice distortions during the precipitation of the metal hydroxide, (c) equilibrium existing between exchangeable and non-exchangeable cations,Bray and De Turk(172), Wood and De Turk (173),(d) fixation of the ions and blocking of exchange positions,Stanford (174).

The maximum exchange capacity in case of aluminum chlorite is due to the maximum tetrahedral substitutions,proved by the least quantity of SiO_2 in this clay. Decrease in the c.e.c. value of ferric chlorite is due to the clogging of the exchange positions by ferric oxide molecules,as shown by Dion (175). Further decrease in c.e.c.values of magnesium and nickel chlorite may be due to the decrease in ionization of the cations because of the lower valency states as compared with Al^{+3} and Fe^{+3} ions,Grim(2) and Marshall(118). Also,there is a possibility of the fixation of these cations by a mechanism similar to that operating for K^{+} ions in illites, as shown by Grim (2),Caillere,Henin and Mering(176).

Stain tests:

Absence of any colouration with the staining solutions with the transformed clays confirms the complete conversion of bentonite structure to some other clay structure.

Dehydration data:

The dehydration curves of bentonite,(Fig.3,curve 1), metal hydroxides,(Fig.4,curves 1-4),and the bentonite-metal hydroxide complexes,(Fig.3,curves 2-5),were used to deduce the dehydration data for metal hydroxide free chlorites, (Fig.5,curves 1-4). The following information is obtained from these curves:

1. There is no loss of water between 100°-200°C in any of the clay samples except bentonite. The dehydration curve of bentonite resembles that of Ross and Hendricks(177), except that the percentage loss of water is more in this case. This water, occuring as interlayer water between the silica sheets, is absent in case of chlorites. The curves for chlorites resemble those given by Nutting(91).
2. Maximum loss of OH water, in case of bentonite, takes place at 600°C, though even at 1000°C the dehydroxylation does not seem to be complete, whereas dehydroxylation is almost complete before 1000°C in case of chlorites. Moreover there is no appreciable loss of water upto about 500°C in case of chlorites. The OH water of chlorites is seen to be driven off in two different stages. This behaviour has been, earlier, observed by Nutting(91) and Orcel(146).
3. Loss of water between 700°-800°C, in case of magnesium and aluminum chlorites, may be due to the loss of mica structure, Brindley and Ali (178). The loss of water between 800°-900°C in case of nickel and ferric chlorites points towards the development of olivine like phases, Grim(2).
4. Dehydration analysis of the metal hydroxides give the following information:

   (a) In case of $Mg(OH)_2$ there is very little loss of water before 300°C but it is completed at 350°C-the temperature at which it passes over to the oxide state.

(b) With $Ni(OH)_2$ the water loss is completed only at 400°C whereby the hydroxide changes over to Bunsenite(NiO).

(c) $Al(OH)_3$ changes over to the oxide form between 200°-400°C.

(d) Major loss of water, in case of $Fe(OH)_3$, takes place between 300°-500°C, whereby it changes over to the oxide form.

The dehydration curves studied, thus, undoubtedly, confirm the transformation of bentonite to chlorite structures.

Differential thermal analysis:

The D.T.A. curve of $Mg(OH)_2$, Fig.7, curve 3, shows a single endothermic peak at 400°C, though the reaction starts at 320°C and goes on till about 450°C. The reported characteristic temperature, by Speil(179), for Brucite, ($Mg(OH)_2$), is 390°C and the peak temperature about 450°C. This characteristic temperature is lowered in presence of $Ca(OH)_2$ and also by the pretreatment of the sample like drying, grinding etc.. $Mg(OH)_2$ is found to change into the oxide form at 350°C from its dehydration curve study.

In the case of nickel hydroxide, (Fig.7, curve 4), a small but a well defined endothermic peak at 135°C indicates the loss of adsorbed water and the second endothermic peak at 390°C, is the temperature at which it completely changes into the oxide form. The observed dehydration temperature for nickel hydroxide is 230°C and it is completed only at 460°C. The maximum temperature for completion of this water loss reported on the basis of dehydration curves is 360°C. This large difference of temperatures perhaps lies in the mode of preparation of $Ni(OH)_2$. The alkali used for the precipitation of nickel chloride in this case is sodium hydroxide and its adsorption on the precipitate cannot be ruled out. This will effect the peak temperature.

The red brown gelatinous precipitate formed upon the addition of alkali to a solution of ferric salt has the composition, Fe_2O_3 nH_2O and is normally referred to as the brown gel‡. Fresh gels all give differential thermal curves with a very strong exothermic peak between 250°-500°C, Mackenzie(100), but the peak temperature and shape vary considerably. In general, high final pH values give broader peaks and higher peak temperatures than low pH values. Also high precipitation temperature gives high peak temperatures. Under these conditions the peak temperature, a sharp one, of 500°C, is not quite abnormal in this case, Fig.7, curve 2. Mackenzie(100) also reports a peak temperature of 500°C where the precipitation pH was 8.5 and the temperature 90°C.

Similarly the first endothermic peak for the loss of adsorbed water has a very high temperature of 220°C as compared to the usual reported value of 150°C. Mackenzie(100) has also reported a temperature of 200°C for this first endothermic peak. All available evidence, Mitchell(180) supports the conclusion that the strong exothermic peak is due to the crystallization of virtually amorphous material to hematite.

The recent work of Mackenzie (100) has proved that all the precipitates from aluminum chloride consist of poorly crystallized boehmite, and has given a well defined endothermic peak at 130°C and the second, a very broad peak, endothermic, at 500°C. The ageing of the sample is shown to lower this second peak temperature. In this case the first peak, Fig.7, curve 1, occurs at 150°C and the second a very sharp one at 400°C. Alumina gels are not analogous to ferric gels, in that very little, if any, amorphous material appears to be present and that consequently there is no exothermic crystallization peak.

From the D.T.A. curve of bentonite, Fig.6, curve 1, it is seen that a well defined single peak is obtained at 160°C which indicates the excess of Ca-bentonite. Other double or shoulder peak is not there which may be because of the other ionic impurities. In this temperature range of 100°-190°C the bulk of water is lost from the interlayer space. From the appearance of the D.T.A. curve the water loss in the 100°-190°C region would seem to cease fairly rapidly but weight loss measurements (dehydration curves, Fig.3, curve 1) show that this is not so and does not clearly distinguish between sorbed and structural water.

The endothermic peak at 700°C is due to the dehydroxylation. The last exothermic peak at 950°C may be due to the formation of new phases. Absence of any endothermic peak at 900°C rules out the possibility of the formation of spinel and suggests a low substitution of Al^{+3} for Si^{+4} ions.

The D.T.A. curve of the synthesized magnesium chlorite, Fig.6, curve 4, gives first a very broad endothermic peak in the temperature range 110°-210°C due to the sorbed water loss. The presence of brucite layer seems to influence this peak shape, (compare curves for $Mg(OH)_2$, Fig.7, curve 3, bentonite, Fig.6, curve 1, and magnesium chlorite, Fig.6, curve 4), suggesting thereby the replacement by Mg^{++} of Al^{+3} ions in the octahedral sheets,(181). The sharp endothermic peak at 400°C is due to the presence of the free hydroxide of magnesium. The second very sharp endothermic peak at 600°C is characteristic of the chlorite mineral,(2), and is due to the delayed decomposition of the brucite layer,sometimes the dehydroxylation of the mica layer is also shown by this very curve. The second endothermic peak after 500°-600°C temperature range usually shown by the natural chlorites or pseudo chlorites is missing in this case,instead a very small endothermic reaction is shown at 730°C,which can be taken as the complete dehydroxylation temperature.As this endothermic peak is immediately followed by an exothermic peak its intensity is bound to be reduced,this peak is because of the structural breakdown of the mica layer followed immediately by recombination and recrystallization of new minerals. The strong and sharp exothermic peak at 800°C is indicative of this new phase developments and this is followed by another exothermic peak at 950°C though not as sharp as in case of bentonite alone. Orcel and Caillere(182), Brindley and Ali(183) and Gallitelli (184) have shown that olivine is formed at this temperature while Nelson (185) has proved the formation of spinel.

The nickel chlorite D.T.A. curve,Fig.6,curve 5, shows first an endothermic reaction in the temperature range 60°-180°C as compared to the range of 110°-180°C for nickel hydroxide,Fig.7,curve 4,and 80°-180°C for bentonite. The second broad endothermic peak at 310°C is because of the nickel hydroxide itself and the third broad endothermic peak is due to dehydroxylation of both the brucite type layer of nickel hydroxide in the chlorite mineral and the mica type sheet. This reaction of dehydroxylation is completed at 740°C which is marked by the appearance of fourth endothermic peak. In this case, unlike magnesium chlorite, there is no immediate exothermic peak following the endothermic peak and also there is only one exothermic peak, the one present in magnesium chlorite at 950°C being absent having merged with the first peak itself and thereby raising the temperature of the first peak from 800°C to 860°C.

The ferric chlorite, Fig.6, curve 3, formed shows, as usual, the first endothermic peak at 110°C followed by a very sharp exothermic peak at 500°C as in case of ferric oxide gel, Fig.7, curve 2. This exothermic peak is immediately followed by an equally sharp endothermic peak, suggesting single step dehydroxylation of the brucite and mica type sheets. This differs from the naturally occuring iron rich variety, bavalite, of decomposition temperature of 470°C, (100). This endothermic peak is now followed by the last exothermic peak with peak temperature at 920°C. Unlike magnesium chlorite, here also we have only one exothermic peak in this temperature range.

In case of aluminum chlorite, Fig.6, curve 2, again as usual, there is an endothermic peak though quite small, in the temperature range 90°-170°C followed by the second sharp and large endothermic peak at 400°C for the aluminum oxide gel, Fig.7, curve 1. The third endothermic peak characteristic of chlorite occurs at 600°C followed by the last exothermic peak at 800°C.

The most interesting features of these curves are:

1. The absence of the second endothermic peak after 600°C.
2. Appearance of an endothermic peak at a temperature of 600°C in case of these synthesized chlorites.

If the deduction of Caillere and Henin(23) that the temperature of second endothermic peak is related to the amount of silicon in the tetrahedral sheet and higher the silicon content, or the less the amount of substitution, the higher the temperature of this peak, is considered, it can be concluded that silicon substitution is the maximum in aluminum chlorite, following the order $Al > Fe > Mg > Ni$ chlorites, supporting the earlier chemical analysis results. The peak temperature of 600°C suggests of a symmetry in the mica sheets of transformed chlorite structures.

From these results, even in the absence of the second endothermic peak to be followed after 600°C endothermic peak, it can, conveniently, be concluded that the transformed structures are chlorites only.

<u>Infrared spectroscopic analysis</u>:

The mulling agent ("Nujol") used in this case gives absorption bands at 2915, 1462, 1376 and 719 $cm.^{-1}$, Rao(165).

In the graph for bentonite(Fig. 8 a, curve 1) apart from the four "Nujol" peaks the following sharp peaks at 3700, 1650 and 670 $cm.^{-1}$ are observed. Adler (163) also reported bands at 3500-3700 and 1650 $cm.^{-1}$ for the adsorbed water in montmorillonite group of clay minerals. The spectrum obtained, in general, resembles with that of Adler(163), except for the fact that in place of a shrp peak at 1040 cm.$^{-1}$, a broad band is observed in this range.

Spectra of the various chlorites, (Fig. 8 b and c) have the common bands at 3700, 920 and 670 cm.$^{-1}$. These have got an extra band at 920 cm.$^{-1}$ in comparison to the bentonite spectrum and point towards the transformation of the original bentonite structure and subsequent development of new groups. This band at 920 cm.$^{-1}$ is due to the O-Al-OH or O-Fe-OH groups like that of nontronites, (107).

The band observed at 1040 cm.$^{-1}$ is due to the Si-O linkages.

These various structures, in the band spectrum range of 800-1200 cm.$^{-1}$, differ in shape as well as the number and intensity of shoulder peaks. This fact can be, successfully, used to distinguish the different amount of the various silicate structures formed or destroyed during this process of precipitation of the metal hydroxide.

Maximum number of shoulder peaks is shown by ferric chlorite (Fig. 8 c, curve 2) and the Si-O band is shown at 1040 cm.$^{-1}$ though the stretching is within the range 990-1100 cm.$^{-1}$. Aluminum chlorite(Fig. 8 c, curve 1)and magnesium chlorite (Fig. 8 b, curve 1) show an equal number of these minor peaks. In aluminum chlorite, the silicon band stretching occurs between 900-1200 cm.$^{-1}$ with the peak at 1060 cm.$^{-1}$ whereas with magnesium chlorite the peak is at 1040 cm.$^{-1}$ and the stretching between 980-1090 cm.$^{-1}$.

Nickel chlorite,(Fig. 8 b, curve 2) shows the least number of peaks with the Si-O band at 1025 cm.$^{-1}$, stretched between 950-1180 cm.$^{-1}$.

Also the position, number and intensity of these minor peaks in the OH stretching band region varies from sample to sample. The intensities of the stretching bands follow~~s~~ the order bentonite > ferric > nickel > magnesium > aluminum chlorite. The aluminum chlorite gives a very broad single band. It may be due to the differences in bonding energy of the OH to the different metals present in these samples.

Another point of interest is that the perturbation of Si-O band is greatest where the perturbation of OH group is larger.

Thus the infrared spectra of these various structures points to the fact that the precipitation of metal hydroxides in between the silica sheets of bentonite leads to the formation of chlorites. Also, various chlorites show the observed difference in behaviour amongst themselves as also from that of bentonite.

X-Ray diffraction analysis:

The diffraction data of the bentonite sample,(Fig.9, curve 1) used is very well comparable to that reported in Card No. 3-0019,(noted from the Index to the X-Ray Powder Data File, 1962, A.S.T.M. special technical publication 48-L). And in a very similar manner the various unheated and heated metal hydroxides diffraction data resemble with their respective Card Nos., given below their data in Table No.10.

From the diffraction data of the unheated magnesium chlorite complex,(Fig.11,curve 1), it can be taken as a mixture of chlorite with a brucite layer plus some free magnesium hydroxide. The third order peak(4.95 A) does not give any unusually high intensity as in the case of the results given by Slaughter and Milne (33);because of the fact that an entirely separate well defined peak for the crystalline free magnesium hydroxide is obtained. The thermal property studied also confirms it to be a chlorite structure. The diffraction diagram of the heated magnesium chlorite,(Fig.11,curve 3), complex shows the pattern for heated magnesium chlorite and free magnesium oxide. The 001 peak is increased in intensity on heating to 600 °C,as expected in case of chlorites,and the other order reflections decrease in intensity to an appreciable degree. Here in this case the ratio of the intensities of these peaks is considered and not their apparent intensities which have been changed due to the presence of free magnesium oxide.

In the case of aluminum chlorite complex, (Fig.9, curve 2), all the lines corresponding to $Al(OH)_3$ and aluminum chlorite are observed. Though Mackenzie (100)expects that the freshly formed gelati~~e~~nous precipitate from aluminum chloride should first change to boehmite,(α AlO(OH)) and upon ageing the boehmite structure should change to bayerite, α $Al(OH)_3$, and finally into gibbsite γ $Al(OH)_3$,but neither in the case of pure $Al(OH)_3$ precipitate,(Fig.9, curve 3),nor that of aluminum chlorite complex,(Fig.9,curve 2), the gibbsite structure has been observed. Both show diffraction patterns similar to that of Bayerite; a number of reasons can be assigned for this, the most important being the state of hydration and ageing as well as the difference in the nature of the precipitant used, (NH_4OH or NaOH). The well developed 14.71 A basal spacing has been obtained in the case of aluminum chlorite but the intensity of 002 reflection relative to that of 001 reflection is more than observed by Slaughter and Milne, (33). It may be due to the difference in the crystalline form of $Al(OH)_3$ precipitated and also its quantity in between the silica sheets. Like magnesium chlorite, this also on heating to 600°C, (Fig.9, curve 4), gives a diffraction pattern in which the 001 reflection increases in intensity and the 002 and 003 order reflections decrease appreciably in intensity.

Nickel chlorite complex, (Fig.12, curve 1), gives lines both for β-$Ni(OH)_2$ and nickel chlorite. The lines for nickel chlorite are comparable with those of Slaughter and Milne(33). However, the 001 reflection, although, of lesser intensity is not completely absent as was observed by them. It is, rather, doubtful, whether, the $Ni(OH)_2$ interlayer formed will completely suppress the first order reflection. Following changes in its diffraction pattern occur on heating it to 600°C, (Fig.12, curve 3), a. intensity of the first order basal reflection is increased considerably, b. 002 reflection decreases drastically in intensity, c. a small band appears in place of the well defined 003 peak, d. 004 order basal spacing completely disappears. Since Slaughter and Milne(33) have not given the diffraction data after heating their nickel chlorite sample, their results cannot be much relied upon.

Ferric hydroxide,(Fig.10,curve 2), as expected,does not show any diffraction pattern due to its amorphous gel like character. Contrary to the work of Slaughter and Milne (33) this sample of ferric chlorite,(Fig.10,curve 1),gives a diffraction pattern although,quite weak in nature,resembling the nickel chlorite complex in some features. The diffraction data obtained after heating ferric chlorite,(Fig.10,curve 3), to 600°C shows the following changes: 001 reflection increases in intensity,weak band changes over to a well defined sharp peak,002 order spacing decreases in intensity and a weak band results in place of the well defined peak for 003 reflection, likewise the intensity of the 004 order decreases considerably-thus establishing the formation of chlorite structure. Ferric hydroxide (free) changes over to ferric oxide and the latter gives its pattern,alongwith that of ferric chlorite.

On the basis of these X-Ray diffraction patterns obtained from the unheated and heated synthesized clay samples,formation of nickel and ferric chlorite has been confirmed beyond any doubt,in extension of the work of Slaughter - Milne (33).

On the basis of all these studies it can,undoubtedly, be concluded that the montmorillonite structure changes over to chlorite structure on precipitation,even of ferric hydroxide or nickel hydroxide in between its silica sheets.

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CHAPTER II

Electrometric titrations and identification of transformed montmorillonite structures(chlorites).

INTRODUCTION

Hydrogen clay and its electrometric titrations:

The use of electrometric titrations,as a means of identifying clay minerals,is well recognized. The technique has been extensively employed,by Paver and Marshall (115), Harmon and Fraulin (186), Mukherjee and Mitra (113,187-192), Grim (2),Adhikari (193) and Chakravarti (194), in case of hydrogen clays or to be more precise H-Al clays. Many workers, particularly,Harward and Colemann (195),Low (196),Goates et al. (197),Aldrich and Buchanan (198), Mitra and Singh(199),have developed methods, of preparing clays,containing varying proportions of Al and H ions,or even pure hydrogen clays and have subjected these to electrometric titrations.

Nature of cation exchange:

Many clays undergo stiochiometric reactions with various reagents. Reactions which involve the cation exchange character of clays, have been reviewed by Hauser (200). Slabough and Culbertson (201) have shown, that the exchangeable hydrogen present in electrodialyzed bentonite systems, is of two principal types-namely,hydrogen ions in the adsorbed layers of the colloidal micelles and hydrogen ions at the cation exchange sites. These ions show primary and secondary characteristics, comparable to a typical ditropic acid.The view generally held,as to the nature of c.e.c., is that most of the exchangeable cations are such monovalent and bivalent cations, of the clay lattice, as balance negative charges, caused by isomorphous replacements in the tetrahedral and octahedral layers of the lattice and are yet accessible to the cations of the contact solution. It fails in case of kaolinite clays, where isomorphous replacement is rather the exception, than the rule. Kelley and Jenny (202) have expressed the view, that kaolinite owes its c.e.c. to H^+ ions, dissociated from the available OH groups, of its crystal lattice. The alternate is, that c.e.c. in kaolin arises from unsatisfied oxygen valencies, developed on the lateral surfaces of the crystals.

Potentiometric titrations of clay minerals:

The results, on the potentiometric titrations of clay suspensions with bases, reveal that the pH variations are, in a manner, comparable to those of weak acids. The work of Mukherjee (113,203,204),Bradfield (205) bears enough testimony to this fact. On the basis of their electrochemical properties, it is possible to differentiate clay minerals from one another. Hydrogen kaolinite shows a dibasic acid character, (122). The ratio of c.e.c. at two inflexions is nearly equal to 2. Mitra (122) ascribed this dibasic character to its possessing two categories of hydroxyl groups, those comprising$(OH)_3$ sheets and those belonging to O_2OH sheets. Hydrogen montmorillonite shows only one inflexion, in its titration curve with NaOH. NaOH titration curves show it to be weak acid, whereas when titrated with $Ba(OH)_2$ or $Ca(OH)_2$ it behaves like a strong acid,(187,190,191,192).

Conductimetric titrations of clay minerals:

The application of conductivity measurements,in investigating clays,may be traced back to the times of Gunther, Schulze and Wiegel, who carried out observations on the electrical conductivity of zeolites. Bradfield (205) and

Baver (206) have shown, that it is easy to locate the equivalence point in dilute clay suspensions, although its realization becomes difficult at higher concentrations. Mital and Bhatacharya (119) have demonstrated, that the inflection points obtained from conductimetric titrations are the same as those obtained from potentiometric methods.

Use of organic solvents:

Chakravarti (207) and more recently Sarkar and Chatterjee (208), have noticed that the inflexion points due to individual minerals often merge with each other,so that all the inflexion points are not separately available in a mixture of pure clay minerals. Moreover the inflexions given by clay acids are not sharp. To overcome such defects, titrations in non aqueous media were suggested by Folin(209). An organic solvent is used to detect separate titration reactions. Over the range of these titrations, two definite reactions were observed by Goates et al. (197). Singhal and Malik (121,210) have successfully used various organic media, for the characterisation of the clay minerals, by their electrometric titrations.

Cation adsorption and electric double layer:

The work of Mitra and Sawhney (211) has shown,that the particle free water extracts, of hydrogen bentonites, contained no titrable acid, thus clearly indicating, that all the acidity of the hydrogen bentonite was associated with the particles of the clay itself. According to the theory of Mukherjee (212,213) the colloidal particles of the sol are surrounded by electrical double layers, whose outer sheets consist of H^+ ions present in a mobile as well as bound or secondarily adsorbed condition. The mobile H^+ ions are responsible for the observed H^+ ion activity of the sol. The c.e.c. of the hydrogen clays depends on many factors, including the considerations of the adsorption of hydroxyl ions and exchange of the cations of the base for the H^+ ions on the surface, types of interaction with the base, which are distinct from the neutralization of acids in true solution.

The sign of the charge on the colloidal precipitate has been found to be reversed by di-and trivalent cations like Ba, Ca and Al ions, but even after the reversal, the concentration of H^+ ions liberated from the interfacial layers continues to increase.

The c.e.c. of hydrogen clays is not a fixed quantity, but changes with the pH and depends on cation effects, associated with the formation of ion pairs on the surface. At comparatively high pH and in the absence of salts the cations are, probably, adsorbed in a dehydrated condition, which accounts for the irregular or specific cation effect.

<u>Preparation of acid clays:</u>

The following four methods are available, for the preparation of acid clays:

1. Acid treatment:- (a) Solubility of clay minerals in acids vary with the nature of the acid, concentration of the acid, the acid-to-clay ratio, the temperature, the duration of the treatment and also the nature of the clay minerals. Hofmann and Endell (214), Glaeser (215) and Mering (216)

have shown that 75-85 % of the total alumina must be removed from montmorillonite lattice before it is completely destroyed.
(b) Mixtures of clay minerals with oxides or hydroxides of aluminum or iron are particularly troublesome to acid treatment.

2. The second procedure is that of simple dialysis. Although equipment has been designed for continuous hot dialysis, the removal of divalent cations is very slow.

3. The technique of electrodialysis was given by Mattson (217) and Bradfield (218). Nutting (219) and Kelley (220) have shown that as the cations are replaced by H^+ ions, aluminum moves from octahedral positions to exchange positions and Hofmann and Giese (221) have shown that, in general, unexchangeable cations are lost from within the lattice, before all the exchangeable cations are replaced by H^+ ions.

4. The fourth method of preparation is by the passage of the clay suspension through columns of acidic cation exchange resins. Some inherent defects in this case are, (a) release of adsorbed mineral acid, (b) release of acidic molecular fragments from the exchanger, (c) clay decomposition, by complex formation between the organic resin exchanger and structural Al or Mg of the clay. Rate of transformation from H-clay to H-Al clay, obtained by ion exchanger technique has been studied by Coleman, (222). Behaviour of clays in neutral salts or alkaline solutions has also been studied, (223,224). Titrations of the resin treated clays show much more strongly acid characters than the electrodialyzed clays. Low (225) has compared these titration curves of

electrodialyzed clays and those of mixtures of HCl and $AlCl_3$.

Concept of exchange capacity:

Exchange in clays involves two functions,(a) the fixed charge on the lattice frame work and ions held in this way give an exchange capacity independent of pH,(b) at the edges of the clay particles ~~an~~ pH dependent exchange function is present, as there are anion and cation exchange sites. To account for the limited reversibility of cations,or the so called "Hysteresis Effect",Wiegner (226) made use of the term "Metastruktur" i.e., presence of sites having different geometries, some of which bind cations more tightly than others. Bower (227) has shown that Cu^{+2}, Mg^{+2}, Zn^{+2}, Fe^{+3}, Th^{+4} ions are retained by a montmorillonite clay in quantities greater than the exchange capacity. It was concluded that hydroxy ions such as $MgOH^{+}$ or $Fe(OH)^{+2}$ were in competition with the normal ions,for exchange sites.

Fixation of ions:

From the structural view point,two cases for fixation can be distinguished, (a) one involving the extension of the octahedral layer beyond the silica layers, (b) the second case involves the reconstitution of the octahedral position, within the confines of the silica layer. Fixation,generally,involves passage of cations from exchange sites to octahedral positions and is,thus,the converse of the type of reaction by which aluminum or iron is rendered exchangeable in acidic clay systems. Probably,this fixation arises due to the formation of hydroxylated ions like $CuOH^{+}$, or $ZnOH^+$ or $ZnCl^+$, (228,229).

Cases of the fixation,adsorption and exchange of anions like the PO_4^{-3} ,OH^- and F^- have also been reported. A good review on this topic of anion exchange and its use in the measurement of surface area of clays has been made by Schofield, (72).

Kelley (75), Marshall (230) and Du Rietz (231) have reviewed the theories of cation exchange,which permit the quantitative expression of exchange data by an equation. Davis (232) has made an attempt to this problem on the basis of kinetic considerations. None of these equation is satisfactory and cannot be universally applied.

<u>Different views on the electrometric titrations of clay minerals</u>:

Recently Mitra,(233), has shown three distinct breaks in the conductimetric titrations of bentonite. According to him upto first break H^+ ions are neutralized, between first and the second break Al^{+3} ions, which occupy exchange sites, are neutralized and between the second and third break the alkali is used up in the reaction with a weak acid component. Previously, Slabough (234) had reported, that montmorillonite titrated in two stages and the first stage was for the neutralization of H^+ ions strong in character and the second break was for weak H^+ ions,from different sites with lesser bonding energies. Lately Harward and Colemann (195) have given the titration curves of montmorillonites and have shown only one stage neutralization of H^+ ions. A two stage titration has been reaffirmed, by Lai et al.(235), who have shown that between the first and second inflexion Al^{+3} ions and not the weak H^+ ions are neutralized. The weak acid being neutralized between the second and third inflexion has been attributed to be due to broken bond hydroxyl groups, or structural OH groups, or a Lewis acid of the type postulated by Miliken, (236). Almost similar observations have been made in the titration curves of micas,illite, attapulgite and nontronite by Mitra and coworkers, (237,238).

EXPERIMENTAL

Preparation of hydrogen clays:

The clay samples were leached continuously with 0.02N HCl, as usual, till the leachate was acidic in reaction, showing the complete dissolution of the free metal hydroxides. Care being taken not to destroy the structure of the clay. The residue was washed, a number of times, with a warm mixture of 1:1 water and ethyl alcohol, until the samples were free from Cl^- ions. Finally the samples were dried in the oven at 105 °C.

quote! A known weight of this clay was added to a measured quantity of double distilled water and was kept shaking for two hours in a mechanical shaker. It was then centrifuged, for half an hour, at 3000 r.p.m. and the colloidal solution so obtained was the hydrogen clay sol obtained by acid leaching.

Resin treated sol:

This hydrogen clay sol was, further, passed through a 30"x 1" column of Amberlite IR-120, which had been earlier regenerated with 1N HCl and washed thoroughly with distilled water, employing the usual recommended precautions for ion exchange, (239). The sol was passed a number of times through the regenerated column, till on repeated treatment no change in the pH of the sol was observed, which was termed the resin treated sol.

Organo sols:

The dry hydrogen clay obtained after acid leaching was dispersed in 90% ethyl alcohol, by shaking in the mechanical shaker, after which it was centrifuged and for resin treatment passed through the ion exchanger, prewashed with alcohol water mixture.

Concentration of the sol:

Concentration of the clay sol was measured in each case by evaporation of a known quantity (about 200-400 ml.) of the sol. Though in case of aquasols a higher concentration could be easily achieved but it had to be kept low to match with the concentration of the alcosol, in which case sols more than 1.0% thick could not be prepared. Dilute sols were in no case obtained by the dilution of a concentrated sol, but were prepared by a fresh dispersion of a calculated amount of the clay in water or alcohol.

Preparation of solutions:

Standard solutions of NaOH were used as titrants. For use in the aqueous medium, aqueous standard solution of NaOH was employed. For carrying out titrations in non aqueous media, standard solution of NaOH in 90% ethyl alcohol was used. Strength of the alkali in both the cases was determined by titration with a solution of standard oxalic acid.

Strength of NaOH was adjusted in each titration according to the concentration of the sol being employed, which was measured as given above, before carrying out the titrations.

The time interval between the preparation of acid clay and each titration was kept as minimum and uniform as possible, to avoid the effects of aluminum movements in H-clays.

Procedure for titrations:

Ten ml. of the sol were added to about fifteen pyrex boiling tubes, each. Varying amounts of standard NaOH in aqueous or alcoholic medium were added and the total volume was made upto 20 ml. by water or alcohol. The tubes were then well corked and kept for about sixty four hours to attain equilibrium.

Before carrying out the actual measurements, preliminary experiments were first conducted, to determine the approximate inflexion points, so that a large number of readings could be taken just before and after the equivalence point. Blank titrations with the two solvents (water and 90% ethyl alcohol) were also carried out, against NaOH in order to ensure accuracy of results, in both the mediums.

Apparatus used:

A Cambridge Bench Type pH meter was used for pH measurements. The readings obtained with this glass calomel assembly were checked with the Pye Students Potentiometer using a hydrogen electrode. Conductivity measurements were carried out with the help of Philips conductivity bridge type PR 9500/90. All measurements were carried out at 30 ± 0.2^{o}C.

Readings in case of the hydrogen electrode were slightly different than the glass electrode for alcoholic medium. This, however, did not interfere with the shape of the curve and the position of the inflection points. Dissociation constants have been calculated from the relationship $pH = pK + \log$ salt / acid so that at half neutralization of the first acidity $pH = pK_1$. Similarly at half neutralization of the second and third acidities pH's at these points have been taken as equivalent to pK_2 and pK_3.

Corresponding information on c.e.c. and pK values as obtained on the basis of conductimetric and potentiometric titrations of the various clays is also included in table number eleven.

RESULTS

TABLE No. 1.

Potentiometric and conductimetric titrations of the acid treated bentonite.

Concentration of the sol used = 0.75%

Quantity of the sol taken = 10.0 ml.

Strength of NaOH = 0.015 N

Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-3} mhos.	pH	Conductivity x 10^{-4} mhos.
		Aqueous		Alcoholic	
0.0	0.0	2.35	6.61	4.69	7.70
1.0	20.0	3.08	5.90	5.55	7.26
2.0	40.0	3.30	5.24	6.00	6.68
3.0	60.0	3.59	4.28	6.31	6.49
4.0	80.0	3.91	3.69	6.54	6.11
4.5	90.0	6.48	3.52	6.76	5.82
4.75	95.0	6.80	4.00	6.92	6.04
5.00	100.0	7.05	4.19	8.70	6.03
5.25	105.0	7.34	4.67	9.75	6.12
5.50	110.0	8.86	4.79	10.10	6.33
5.75	115.0	9.17	5.53	10.36	6.49
6.00	120.0	9.30	6.02	10.54	6.72
6.50	130.0	9.55	7.49	10.78	7.37
7.00	140.0	9.74	7.91	10.91	7.68
8.00	160.0	10.08	1.02×10^{-2}	11.32	8.50
		Fig.1, Curve 1.	Fig.1, Curve 3.	Fig.2, Curve 1.	Fig.2, Curve 3.

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF BENTONITE IN ALCOHOLIC MEDIUM

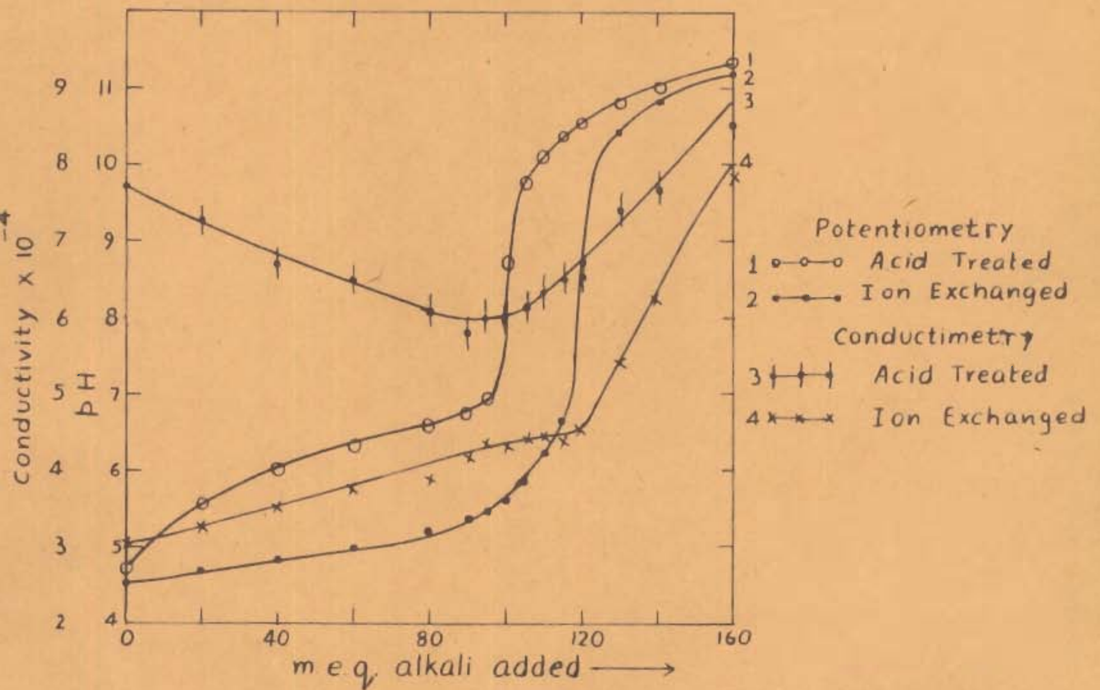


FIG · 2

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF BENTONITE IN AQUEOUS MEDIUM

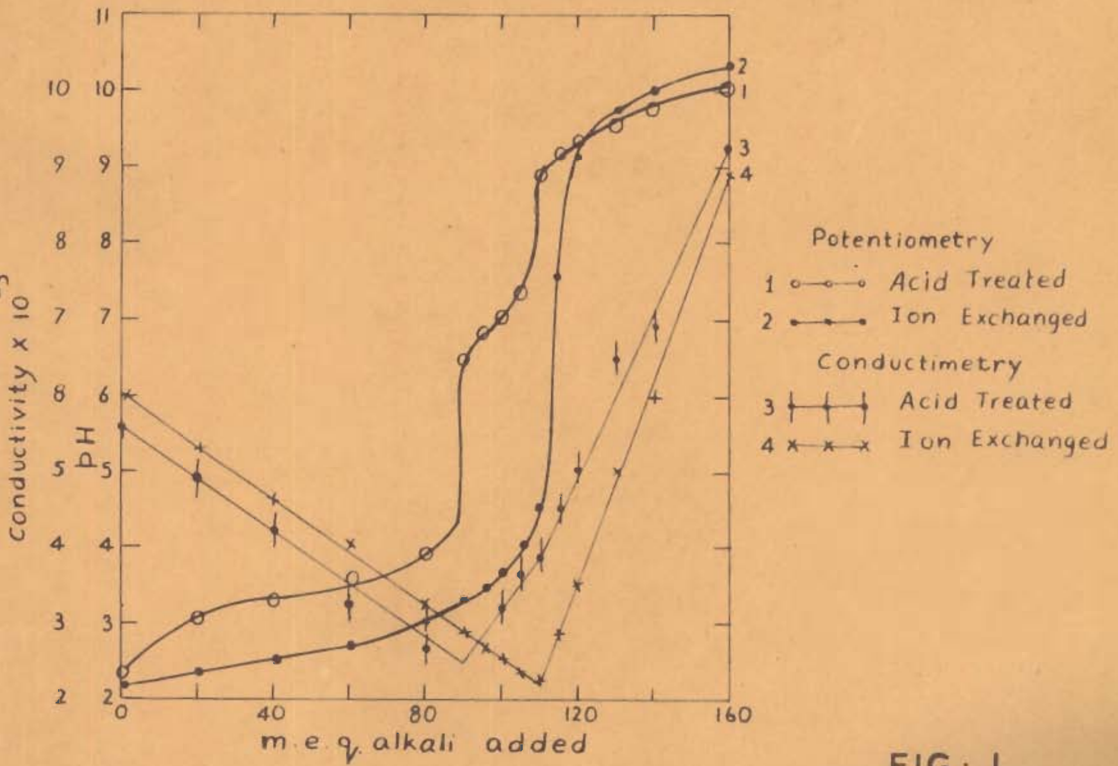


FIG · 1

TABLE No.2

Potentiometric and conductimetric titrations of the resin treated bentonite.

Concentration of the sol = 0.74 %
Amount of the sol taken = 10.0 ml.
Strength of NaOH = 0.0148 N.
Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity $\times 10^{-3}$ mhos.	pH	Conductivity $\times 10^{-4}$ mhos.
		Aqueous		Alcoholic	
0.0	0.0	2.18	6.98	4.52	2.99
1.0	20.0	2.36	6.30	4.69	3.25
2.0	40.0	2.52	5.57	4.82	3.49
3.0	60.0	2.69	5.04	4.98	3.76
4.0	80.0	3.03	4.23	5.19	3.88
4.5	90.0	3.31	3.88	5.35	4.12
4.75	95.0	3.45	3.70	5.44	4.31
5.00	100.0	3.66	3.53	5.60	4.29
5.25	105.0	4.02	3.36	5.86	4.35
5.50	110.0	4.51	3.24	6.23	4.40
5.75	115.0	7.65	3.85	6.64	4.35
6.00	120.0	9.13	4.51	8.53	4.52
6.50	130.0	9.76	6.00	10.41	5.38
7.00	140.0	9.99	6.99	10.83	6.22
8.00	160.0	10.30	9.85	11.15	7.80
		Fig.1, Curve 2.	Fig.1, Curve 4.	Fig.2, Curve 2.	Fig.2, Curve 4.

TABLE No.3.

Potentiometric and conductimetric titrations of the acid treated aluminum chlorite.

Concentration of the sol = 0.77 %

Amount of the sol taken = 10.0 ml.

Strength of NaOH = 0.00385 N.

Total volume = 25.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-5} mhos.
		Aqueous		Alcoholic	
0.0	0.0	2.73	2.29	5.93	1.44
1.0	5.0	3.32	2.05	6.31	1.54
2.0	10.0	3.64	1.87	6.48	1.73
3.0	15.0	3.85	1.64	6.59	1.95
4.0	20.0	3.98	1.52	6.72	2.36
5.0	25.0	4.11	1.36	6.86	2.17
5.5	27.5	4.63	1.31	6.94	2.24
6.0	30.0	5.57	1.31	7.07	2.38
6.5	32.5	6.86	1.35	8.30	2.56
7.0	35.0	7.64	1.45	9.58	2.73
7.5	37.5	8.05	1.57	9.81	2.87
8.0	40.0	8.48	1.76	9.93	3.10
8.5	42.5	8.82	1.92	10.20	3.26
9.0	45.0	9.15	2.01	10.57	3.75
9.5	47.5	9.34	2.14	10.88	4.78
10.0	50.0	9.72	2.43	10.99	5.50
11.0	55.0	10.20	9.94	11.28	6.89
		Fig.3, Curve 1.	Fig.3, Curve 3.	Fig.4, Curve 1.	Fig.4, Curve 3.

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF ALUMINIUM CHLORITE IN ALCOHOLIC MEDIUM

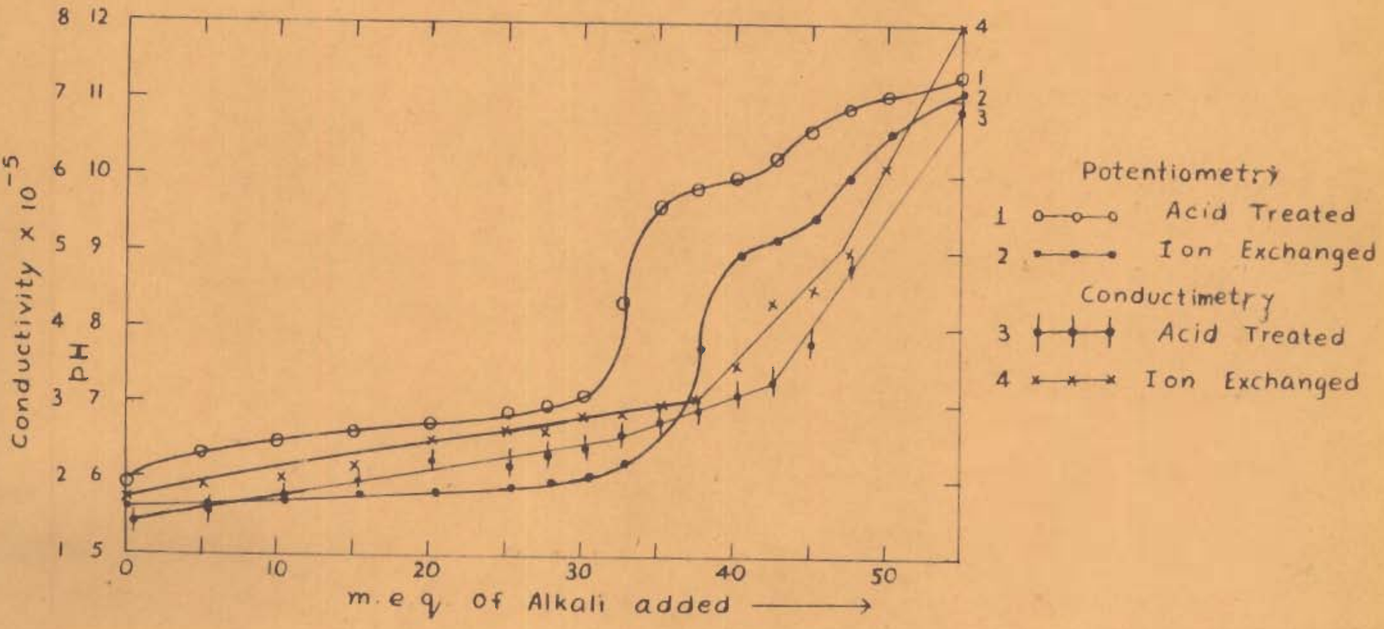


FIG. 4

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF ALUMINIUM CHLORITE IN AQUEOUS MEDIUM

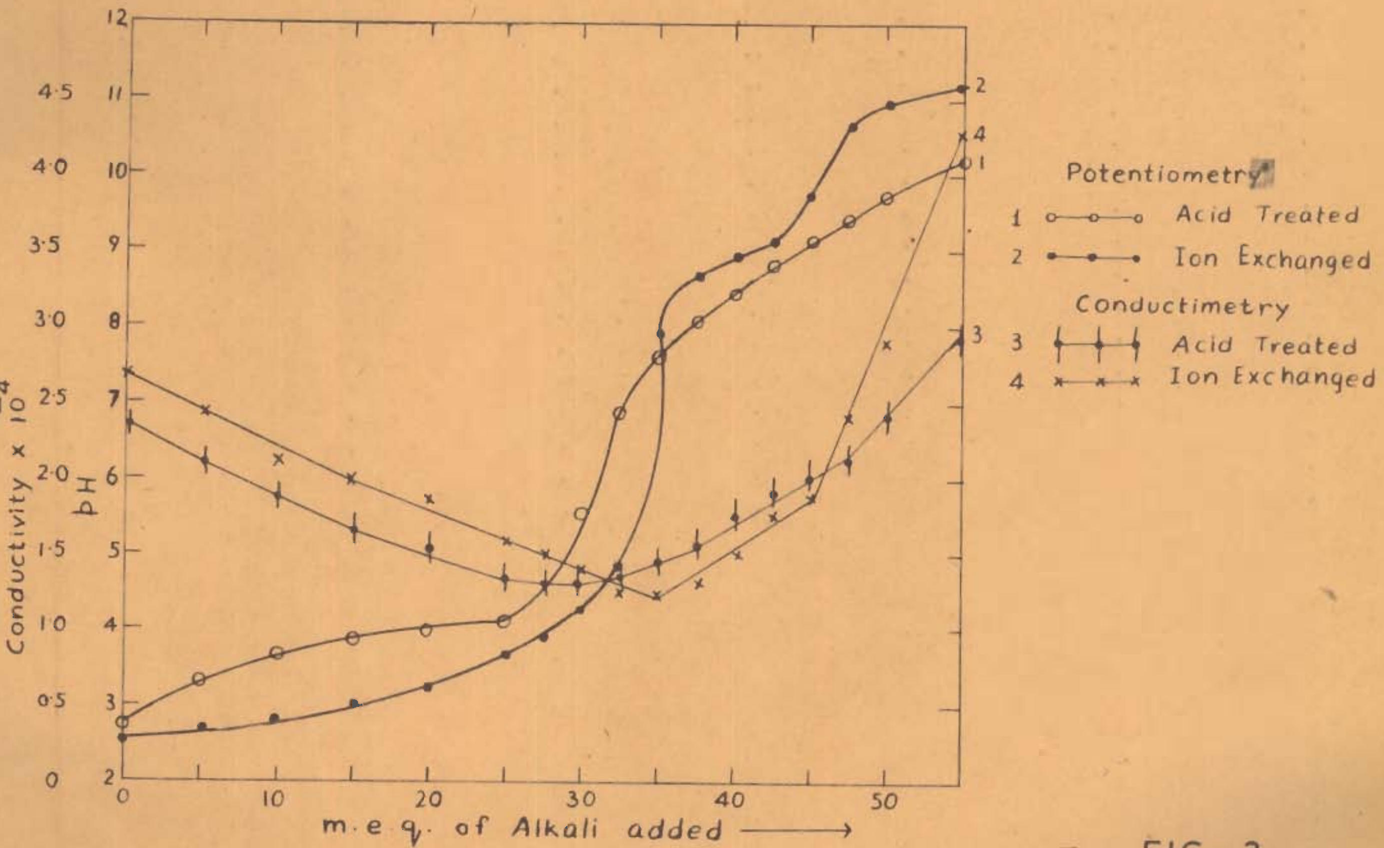


FIG. 3

TABLE No.4.

Potentiometric and conductimetric titrations of the resin treated aluminum chlorite.

Concentration of the sol = 0.756 %

Amount of the sol taken =10.0 ml.

Strength of NaOH = 0.00378 N.

Total volume =26.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-5} mhos.
		Aqueous		Alcoholic	
0.0	0.0	2.52	2.66	5.63	1.75
1.0	5.0	2.69	2.43	5.67	1.90
2.0	10.0	2.78	2.10	5.70	2.00
3.0	15.0	3.03	1.99	5.80	2.17
4.0	20.0	3.24	1.83	5.85	2.51
5.0	25.0	3.62	1.57	5.88	2.60
5.5	27.5	3.89	1.48	5.94	2.60
6.0	30.0	4.24	1.40	6.03	2.78
6.5	32.5	4.76	1.25	6.19	2.80
7.0	35.0	7.90	1.23	6.42	2.98
7.5	37.5	8.68	1.31	7.71	3.05
8.0	40.0	8.91	1.49	8.95	3.47
8.5	42.5	9.13	1.75	9.13	4.30
9.0	45.0	9.74	1.87	9.43	4.46
9.5	47.5	10.65	2.41	9.96	5.00
10.0	50.0	10.96	2.68	10.52	6.11
11.0	55.0	11.19	4.30	11.04	7.98
		Fig.3, Curve 2.	Fig.3, Curve 4.	Fig.4, Curve 2.	Fig.4, Curve 4.

TABLE No.5.

Potentiometric and conductimetric titrations of the acid treated ferric chlorite.

Concentration of the sol = 0.72 %

Amount of the sol taken = 10.0 ml.

Strength of NaOH = 0.0036 N.

Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-6} mhos.
		Aqueous		Alcoholic	
0.0	0.0	3.19	4.00	7.04	4.08
1.0	5.0	4.38	2.87	7.62	4.11
2.0	10.0	4.81	1.75	7.83	4.19
3.0	15.0	5.29	0.57	7.97	4.21
3.5	17.5	7.66	0.08	8.16	4.28
4.0	20.0	9.10	0.22	9.39	4.35
4.5	22.5	9.41	0.28	9.78	4.54
5.0	25.0	9.62	0.50	9.88	4.86
5.5	27.5	10.20	0.53	9.96	5.25
6.0	30.0	11.08	1.61	10.44	5.73
6.5	32.5	11.27	2.78	11.23	6.35
7.0	35.0	11.38	4.00	11.52	6.78
8.0	40.0	11.48	5.67	12.10	7.39
		Fig.5, Curve 1.	Fig.5, Curve 3.	Fig.6, Curve 1.	Fig.6, Curve 3.

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF FERRIC CHLORITE IN ALCOHOLIC MEDIUM

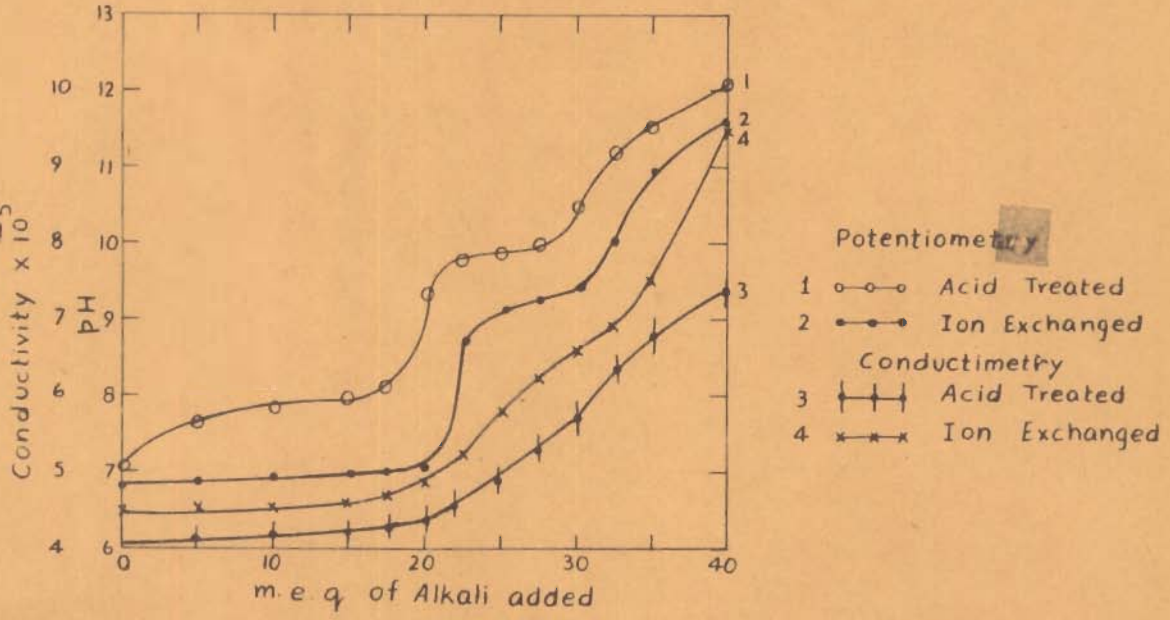


FIG. 6

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF FERRIC CHLORITE IN AQUEOUS MEDIUM

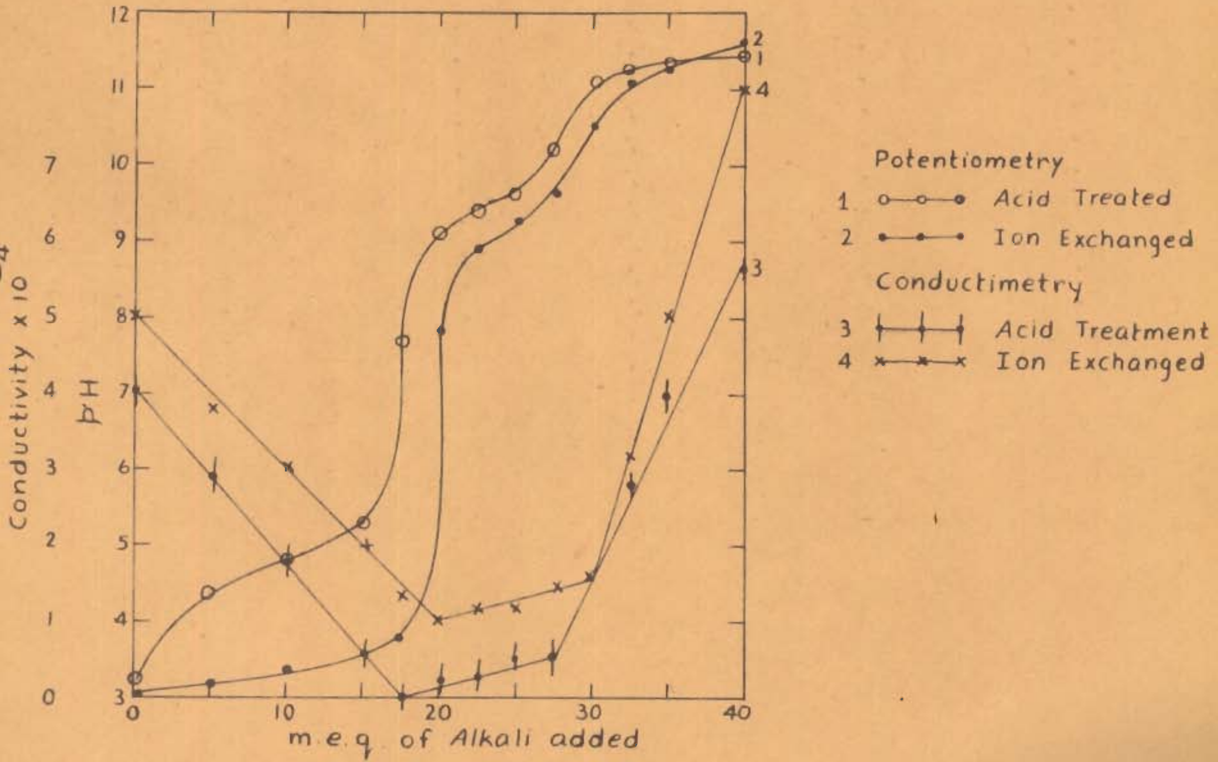


FIG. 5

TABLE No. 6.

Potentiometric and conductimetric titrations of the resin treated ferric chlorite.

Concentration of the sol = 0.70 %

Amount of the sol taken = 10.0 ml.

Strength of NaOH = 0.0035 N.

Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-5} mhos.
		Aqueous		Alcoholic	
0.0	0.0	3.02	4.99	6.81	4.48
1.0	5.0	3.19	3.78	6.88	4.50
2.0	10.0	3.35	3.00	6.93	4.52
3.0	15.0	3.57	1.99	6.99	4.60
3.5	17.5	3.79	1.32	7.02	4.68
4.0	20.0	7.82	1.02	7.11	4.85
4.5	22.5	8.89	1.15	8.68	5.20
5.0	25.0	9.25	1.14	9.12	5.75
5.5	27.5	9.66	1.47	9.29	6.21
6.0	30.0	10.48	1.55	9.44	6.58
6.5	32.5	11.07	3.29	10.06	6.89
7.0	35.0	11.31	5.02	10.95	7.51
8.0	40.0	11.62	7.83	11.67	9.48
		Fig.5, Curve 2.	Fig.5, Curve 4.	Fig.6, Curve 2.	Fig.6, Curve 4.

TABLE No. 7.

Potentiometric and conductimetric titrations of the acid treated magnesium chlorite.

Concentration of the sol = 0.81 %

Amount of the sol taken = 10.0 ml.

Strength of NaOH = 0.00405 N.

Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-5} mhos.
		Aqueous		Alcoholic	
0.0	0.0	3.64	4.27	7.16	4.18
1.0	5.0	4.46	2.65	7.97	4.33
1.5	7.5	4.80	2.21	8.32	4.40
2.0	10.0	8.92	1.53	9.75	4.49
2.5	12.5	9.66	1.60	10.81	4.55
3.0	15.0	9.98	1.79	11.20	4.78
3.5	17.5	10.14	1.70	11.47	5.49
4.0	20.0	10.97	1.88	12.26	5.53
4.5	22.5	11.63	2.39	12.95	6.49
5.0	25.0	11.81	3.32	13.17	7.00
6.0	30.0	11.88	4.84	13.49	8.58
		Fig.7, Curve 1.	Fig.7, Curve 3.	Fig.8, Curve 1.	Fig.8, Curve 3.

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF MAGNESIUM CHLORITE IN ALCOHOLIC MEDIUM

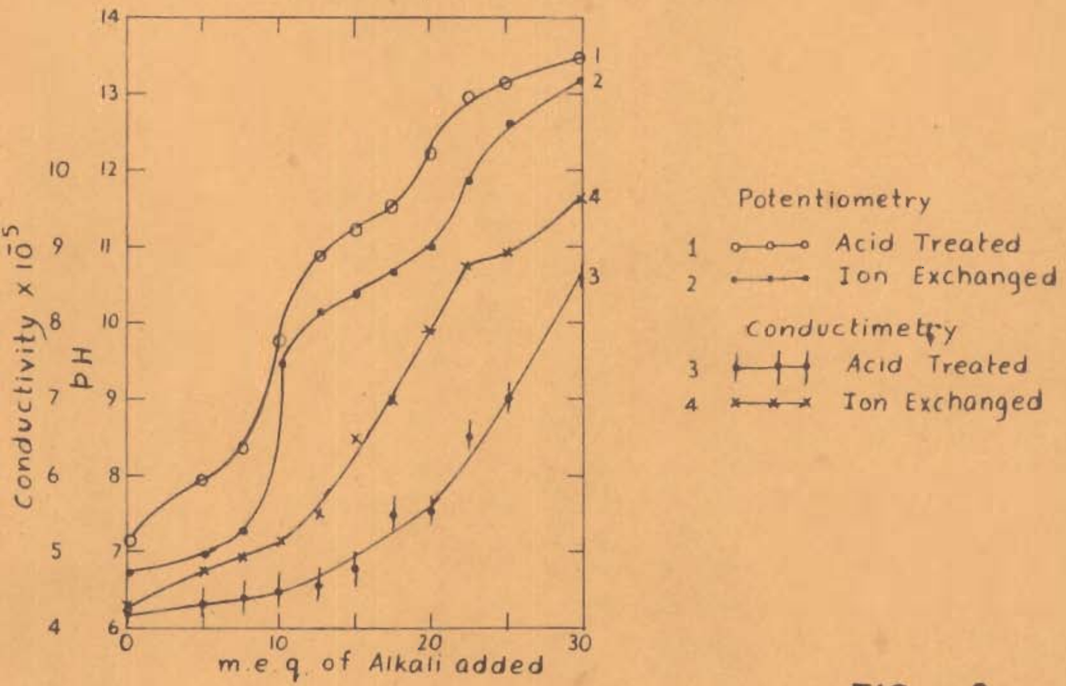


FIG · 8

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF MAGNESIUM CHLORITE IN AQUEOUS MEDIUM

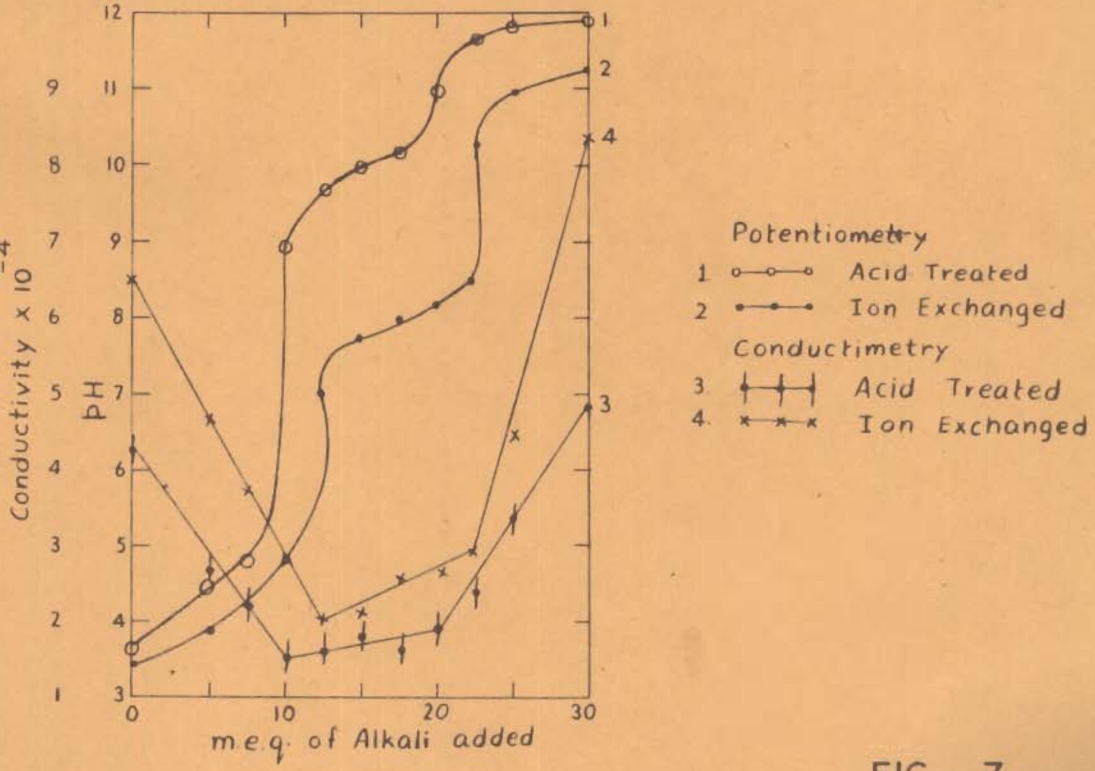


FIG · 7

TABLE No. 8.

Potentiometric and conductimetric titrations of the resin treated magnesium chlorite.

Concentration of the sol = 0.77 %
Amount of the sol taken = 10.0 ml.
Strength of NaOH = 0.00385 N.
Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-5} mhos.
		Aqueous		Alcoholic	
0.0	0.0	3.44	6.48	6.73	4.31
1.0	5.0	3.87	4.61	6.99	4.77
1.5	7.5	4.23	3.70	7.25	4.96
2.0	10.0	4.81	2.82	9.48	5.15
2.5	12.5	6.97	2.01	10.08	5.49
3.0	15.0	7.72	2.09	10.37	6.48
3.5	17.5	7.98	2.53	10.65	6.97
4.0	20.0	8.19	2.58	10.96	7.93
4.5	22.5	10.20	2.90	11.88	8.70
5.0	25.0	10.93	4.46	12.57	8.94
6.0	30.0	11.25	8.35	13.18	9.62
		Fig.7, Curve 2.	Fig.7, Curve 4.	Fig.8, Curve 2.	Fig.8, Curve 4.

TABLE No.9.

Potentiometric and conductimetric titrations of the acid treated nickel chlorite.

Concentration of the sol = 0.72 %

Amount of the sol taken = 10.0 ml.

Strength of NaOH = 0.00216 N.

Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-5} mhos.
		Aqueous		Alcoholic	
0.0	0.0	4.18	6.67	6.64	5.08
1.0	3.0	5.06	6.18	7.30	5.14
2.0	6.0	5.61	5.92	7.68	5.27
2.5	7.5	6.87	5.59	7.99	5.31
3.0	9.0	7.55	5.50	8.98	5.36
3.5	10.5	8.51	5.27	9.62	5.65
4.0	12.0	9.00	5.50	9.83	5.84
4.5	13.5	9.19	5.64	10.00	5.69
5.0	15.0	9.34	5.71	10.17	5.98
5.5	16.5	9.86	5.93	10.36	6.23
6.0	18.0	10.62	6.25	11.14	6.46
6.5	19.5	10.95	6.76	11.95	6.97
7.0	21.0	11.17	7.00	12.36	7.23
8.0	24.0	11.48	7.97	12.87	9.68
		Fig.9, Curve 1.	Fig.9, Curve 3.	Fig.10, Curve 1.	Fig.10, Curve 3.

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF NICKEL CHLORITE IN ALCOHOLIC MEDIUM

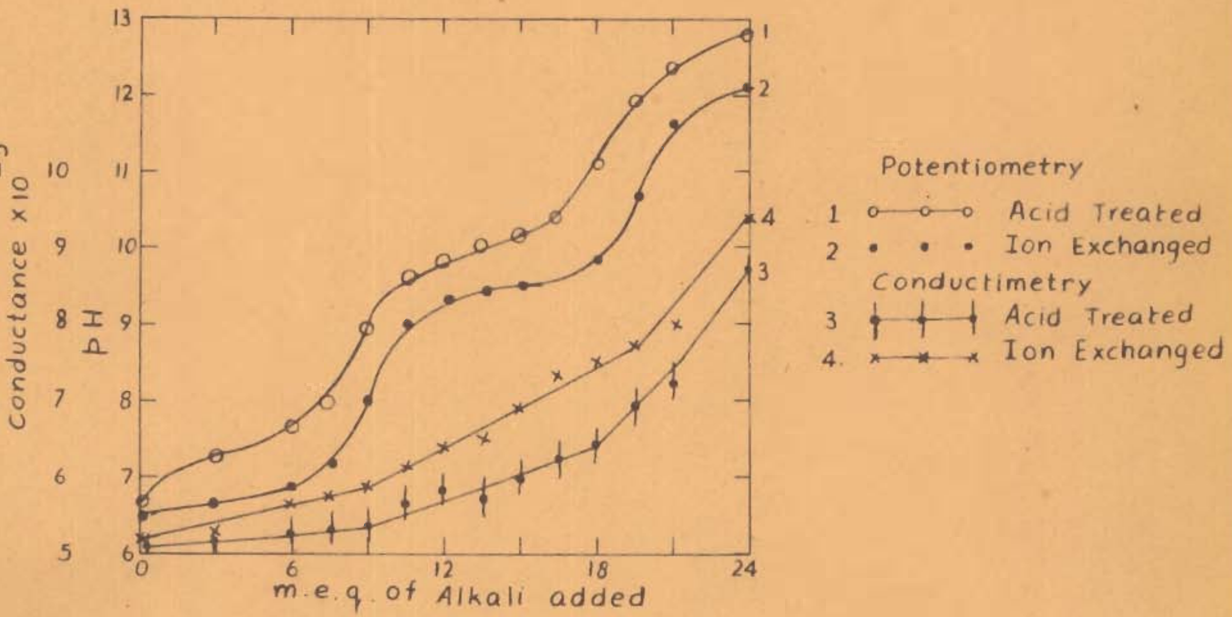


FIG. 10

POTENTIOMETRIC AND CONDUCTIMETRIC TITRATIONS OF NICKEL CHLORITE IN AQUEOUS MEDIUM

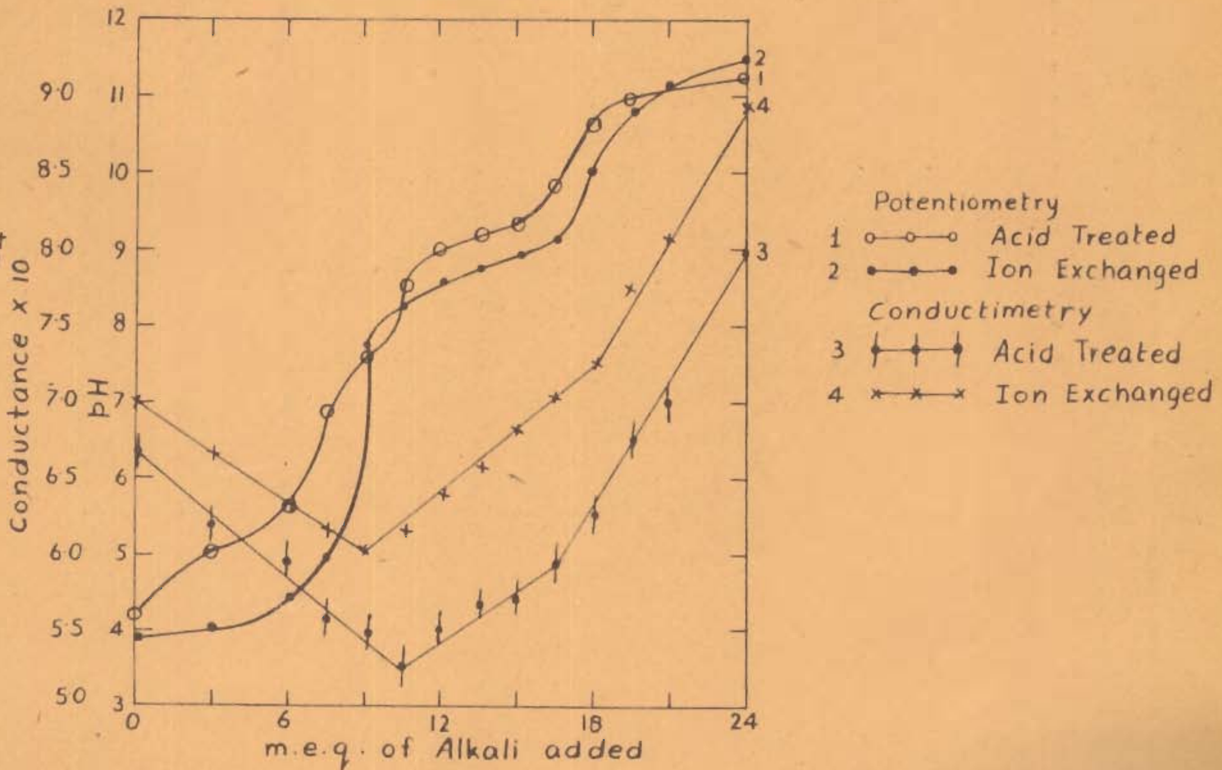


FIG. 9

TABLE No.10

Potentiometric and conductimetric titrations of the resin treated nickel chlorite.

Concentration of the sol = 0.705 %

Amount of the sol taken = 10.0 ml.

Strength of NaOH = 0.002115 N.

Total volume = 20.0 ml.

Vol. of NaOH ml.	M.e.q. of alkali per 100 g. clay.	pH	Conductivity x 10^{-4} mhos.	pH	Conductivity x 10^{-5} mhos.
		Aqueous		Alcoholic	
0.0	0.0	3.86	6.99	6.49	5.19
1.0	3.0	4.05	6.66	6.64	5.25
2.0	6.0	4.42	6.31	6.86	5.61
2.5	7.5	4.97	6.16	7.19	5.74
3.0	9.0	7.71	6.00	8.00	5.88
3.5	10.5	8.23	6.14	9.01	6.12
4.0	12.0	8.52	6.41	9.27	6.39
4.5	13.5	8.75	6.52	9.39	6.49
5.0	15.0	8.90	6.80	9.50	6.91
5.5	16.5	9.11	7.02	9.58	7.30
6.0	18.0	10.13	7.24	9.86	7.48
6.5	19.5	10.76	7.73	10.61	7.68
7.0	21.0	11.18	8.07	11.60	7.99
8.0	24.0	11.49	8.90	12.12	9.37
		Fig.9, Curve 2.	Fig.9, Curve 4.	Fig.10, Curve 2.	Fig.10, Curve 4.

TABLE No. 11

Cation exchange capacity and the corresponding pK values of the clay samples as obtained from figures 1-10.

Inflexion	Method	Bentonite			
		Resin treated		Acid leached	
		Aqueous	Alcoholic	Aqueous	Alcoholic
1.	pH	115(2.7)	120(5.0)	90(3.4)	100(6.2)
	Cond.	120	120	90	95
2.	pH	-	-	110(7.0)	-
	Cond.	-	-	110	-
		Aluminum chlorite			
1.	pH	35(3.1)	37.5(5.8)	30(3.8)	32.5(6.6)
	Cond.	35	37.5	30	32.5
2.	pH	47(9.0)	47.5(9.2)	-	42.5(10.0)
	Cond.	45	47.5	-	42.5
		Ferric chlorite			
1.	pH	20(3.35)	22.5(6.9)	17.5(4.7)	19(7.8)
	Cond.	20	20	17.5	20
2.	pH	30(6.6)	32.5(7.2)	27.5(6.3)	30(9.8)
	Cond.	30	32.5	27.5	30
		Magnesium chlorite			
1.	pH	12.0(4.1)	10.0(5.0)	10.0(4.5)	10(7.95)
	Cond.	12.5	10.0	10.0	10
2.	pH	22.5(8.0)	22.5(10.5)	20.0(9.9)	20(11.2)
	Cond.	22.5	22.5	20.0	20
		Nickel chlorite			
1.	pH	9.0(4.2)	9.0(6.7)	7.5(5.2)	-
	Cond.	9.0	9.0	-	-
2.	pH	-	-	10.5(7.6)	9.0(7.5)
	Cond.	-	-	10.5	9.0
3.	pH	18.0(8.7)	19.5(9.5)	17.5(9.2)	18.0(10.0)
	Cond.	18.0	19.5	17.5	18.0

DISCUSSION

The electrometric titrations of acid leached and resin treated hydrogen clays, carried out both in the aqueous and alcoholic media, not only provide useful information about the nature of the electrical double layers,in montmorillonite structure, but are also helpful in explaining the complex electrometric behaviour of modified clay structures.

A perusal of the conductimetric and potentiometric titration curves (Figs.1 and 2) of the two hydrogen bentonites would reveal the following remarkable differences between the two:

The acid treated clay gives two inflexion points (Fig.1, Curve 1) while the resin treated clay (Fig.1,Curve 2)gives only one inflexion point. Moreover, the second inflexion point of the acid treated clay disappears in the alcoholic medium (Fig.2,Curve 1). Besides,the c.e.c. as determined from the second inflexion point of the acid leached bentonite (110 m.e.q. per 100 gm.clay) is almost equal to the value obtained from the single inflexion point in the resin treated clay (115 - 120 m.e.q. per 100 gm.clay). There,however, exists a large difference in the pK values in the aqueous medium, where the pK values vary from 2.7 to 7.0, but this difference is very much levelled in the alcoholic medium, where only one inflexion corresponding to the pK values of 5.0 and 6.2 is obtained. These differences between the pK values in the aqueous and alcoholic media are understandable, but as to why only one inflexion point is obtained in the resin treated clay, where as two inflexion points with pK values so far apart are observed in acid leached clay, needs further clarification.

The fact that the values of c.e.c. are not materially changed, points towards the fact that the removal of H^+ ions does not take place in one stage, in the acid leached clay. The picture as regards the orientation of Al^{+3} and H^+ ions in these two systems may be taken as follows: The surface of the acid leached clay does not contain simply H^+ ions in the Gouy and Stern part of the double layers, (the number of cations in clays are more in the Stern Layer than Gouy Layer), but also aluminum ions. Since acid leaching is not able to exchange all the cations of the original clay by hydrogen ions, the first inflexion, therefore, is for the neutralisation of the H^+ ions, or the alumino-silicic acid (much stronger than silicic acid), or both, whereas the second inflexion point can be due to the interaction of the liberated aluminum ions with hydroxyl ions. This is supported by the fact that the first inflexion point lies in the pH range 4.5-6.5, typical for acid base titration curves, and the second inflexion point lies in the fairly basic pH range 7.5 - 9.0, conducive to the formation of domains of hydroxide, incorporating the exchangeable aluminum ions (with the probable formation of aluminous chlorite). These results are in conformity with the data of Lai et al. (235) and Mitra (233).

As regards the resin treated clay, it can be said that the aluminum ions are not only liberated from the octahedral layers, but with increasing acidity the displacements from the tetrahedral layers also take place. The observed inflexion point would, therefore, give the total aluminum and hydrogen clay acidity. The values of cation exchange capacity, both in the aqueous and the alcoholic media are almost the same. The difference in pK values can be attributed to the change from the aqueous to the alcoholic media. Several views, such as the replacements in the tetrahedral and octahedral layers, the difference in the bonding energies of the ions associated with these two layers, complete substitution in the tetrahedral layer, weak forces operating in octahedral substitutions, (118), different bonding energies associated with the location of ions on the flake surfaces, edges and corners (237), or the chemical concept of the dissociation of Si-OH linkages (240) have been put forward from time to time to explain the orientation of Al^{+3} and H^{+} ions in the different layers, but the fact remains that the exchangeable ones, irrespective of the lattice source, can be estimated, both potentiometrically and conductimetrically, provided sufficient time is allowed for the clay particles to remain in contact with the acid, during its conversion to the hydrogen clay. This can be very well achieved by resin treatment method, as is evident from what has been said above, regarding the electrometric behaviour of resin treated and acid leached bentonite.

Out of the four transformed bentonite structures (chlorites), the behaviour of aluminum chlorite is different from that of ferric, magnesium and nickel chlorite. Here not only sharp inflexion points are not realized, but in case of the acid treated clay the second inflexion point in the aqueous medium, (Fig.3, Curve 1), ceases to exist. This may be attributed to the unique position of aluminum in clay minerals. The aluminum ion by virtue of its size can accomodate itself both in tetrahedral and octahedral coordination with oxygen, forming both strong and weak bonds. Besides, its hydroxide is amphoteric in character, with the result that its colloid chemical properties are very much pH-dependent. The two inflexion points in case of resin treated aluminum chlorite (Fig.3, Curve 2), lying in the pH range 4.5 - 8.5 and 9.0 - 10.5 in case of aqueous medium and 6.5 - 9.0 and 9.2 - 10.8 in case of alcoholic medium, (Fig.4, Curve 2), give almost the same c.e.c. values in both the aqueous and alcoholic media. A similar behaviour is observed in the case of acid leached aluminum chlorite. Here the first inflexion point lies in the pH range 7.0 - 9.8 and the second in the pH range 10.0 - 11.0 in alcoholic medium, (Fig.4, Curve 1), whereas the pH range of the single inflexion in aqueous medium is 4.0 - 8.0, (Fig.3, Curve 1). The first inflexion point can be compared to an inflexion for an acid base titration, involving neutralisation of H^+ ions, (aluminosilicic acid and oxy salts of aluminum), present at low pH values. The pH range for these titrations is almost the same as for the first inflexion point in hydrogen bentonite(4.5 - 6.5 for bentonite and 4.0 - 8.0 for aluminum chlorite).

The second inflexion point may be due to the neutralisation of hydrogen ions, present in the chlorite like interlayers. Since it is difficult to distinguish the octahedral aluminum of the clay from aluminum hydroxide, the second inflexion point is not sharp and in case of acid treated clay requires the "Levelling Effect", in alcoholic medium. It has been said that Al - H clays of this type contain Si - O -Al linkages, the acid treatment would, thus, involve the replacement of exchangeable aluminum by hydrogen ions. The second inflexion point is, thus, due to the neutralisation of the clay acidity arising in this way.

As regards the electrometric behaviour of the other three clays, the pH range are as follows:

1. Ferric chlorite: -
   a. Acid leached: (i) aqueous medium, (Fig.5, Curve 1); 5.0-9.0 and 9.5-11.2, (ii) alcoholic medium, (Fig.6, Curve 1); 8.0-9.8 and 10.0-11.5.
   b. Resin treated: (i) aqueous medium, (Fig.5, Curve 2); 3.5-9.0 and 9.2-11.2, (ii) alcoholic medium, (Fig.6, Curve 2); 7.0-9.2 and 9.5-11.5.
2. Magnesium chlorite:-
   a. Acid leached: (i) aqueous medium, (Fig.7, Curve 1); 4.8-9.7 and 10.0-11.6, (ii) alcoholic medium, (Fig.8, Curve 1); 8.0-11.0 and 11.5-13.2.

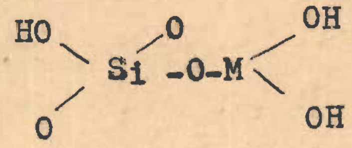
b. Resin treated: (i) aqueous medium,(Fig.7,Curve 2); 4.0-7.5 and 8.0-11.2, (ii) alcoholic medium,(Fig.8, Curve 2);7.0-10.2 and 11.0-12.5.

3. Nickel chlorite:-

a. Acid leached: (i) aqueous medium,(Fig.9,Curve 1); 5.2-7.5 and 7.5-9.0 and 9.3-11.1,(ii) alcoholic medium,(Fig.10,Curve 1); 7.8-10.0 and 10.2-12.0.

b. Resin treated: (i) aqueous medium,(Fig.9,Curve 2); 4.5-8.5 and 9.0-11.0,(ii) alcoholic medium,(Fig.10, Curve 2); 6.8-9.3 and 9.6-12.1.

In these cases the first inflex~~t~~ion point represents the neutralization of H^+ ions,aluminosilicic acid and oxy salts (only in case of ferric chlorite). Second inflexion point which in every case falls in quite a high pH range (specially in the case of magnesium chlorite)may be due to the dissociation of hydroxylic hydrogen from the acidic OH groups, of the metal or from Si-OH linkages, or both, or of the following type of structures,



M stands for metal ions.

The sharpness of the second inflexion point in these three clays is due to the greater solubilities of their metal hydroxides than $Al\ (OH)_3$,leading to their better incorporation in the montmorillonite structure. This is most evident with magnesium chlorite, due to the maximum solubility of magnesium hydroxide.

The reasons for the different c.e.c. of these transformed structures have already been discussed in the first chapter. The fall of c.e.c. from about 90.0 m.e.q. per 100 gm.clay in case of bentonite to about 18.0 m.e.q. per 100 gm. clay in case of nickel chlorite confirms the transformation of the montmorillonite structure into chlorite structure. Another interesting fact arises out of these studies- and it is that the difference in c.e.c. between the first and the second inflexion is 10 m.e.q. per 100 gm.clay irrespective of the nature of the clay used.

The electrometric titrations also provide a method of differentiating between chlorites and other clay minerals. Chlorite like structures give two inflexion points as compared to only one in case of bentonite. Also unlike the monobasic montmorillonites, where the inflexion occurs almost in the alkaline range, chlorites behave as dibasic acid; and at the same time these can be differentiated from the dibasic montmorillonites reported by Mitra (191), where the ratio of c.e.c!s at the two inflexion points is greater than 2.0.

These structures can also be distinguished from kaolinites,inspite of their similar dibasic acid character, from the fact that unlike kaolinites, the ratio of c.e.c. at the two inflexions is not equal to 2.0 and that the first inflexion occurs in a much wider and acidic pH range- usually 4.0-8.0, than the pH range of 7.0-8.0 of kaolinite.

These transformed bentonite structures (chlorites) can also be differentiated from illites. Illites always behave like tribasic acids giving three inflexion points. So also these structures can be differentiated from attapulgite, nontronite and other muscovites,(237,238), as all these latter give three inflexions and also the c.e.c. values are generally larger than the corresponding values for chlorites.

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CHAPTER III

Rheological properties of transformed montmorillonite structures (chlorites).

INTRODUCTION

Viscometric studies:

The influence of peptization and flocculation on the flow behaviour or the rheology of suspensions are of utmost importance in technology, industry and agriculture. The degree of stability, of a dispersed system, governs the pumpability of drilling fluids, the proper levelling of brush marks in painting and the occurence of landslides etc..

The viscosity of colloidal systems provides an expression of three sets of interactions: those between suspended particles, those between suspended particles and dispersion medium and those between molecules of the dispersion medium themselves.

Hydrophobic and hydrophilic sols:

Philippof (241) has enumerated a number of factors, which contribute to the viscosity of a suspension, notable among them being the nature and concentration of the suspension, the size and shape of the particles and the influence of foreign ions on it. The latter effects have been extensively investigated both for hydrophobic and hydrophilic colloidal solutions and although these are more pronounced in hydrophilic sols where influences, like hydration, electroviscous effect, interfacial tension etc., play a dominant role; they are by no means insignificant in the case of hydrophobic systems especially those formed from big molecules, with polar groups, or those exhibiting great tendency towards gelation.

The recent work of Nash,(242),characterizing clays possessing both hydrophobic and hydrophilic ends (properties),and the work on the gelation of prussian blue (243), or metallic tungstates (244), and molybdates (245) lends support to this fact.

Apart from the notable work on various colloidal systems, of Henry (246), Kruyt (247),Marshall (248) and the conclusions arrived at by Pauli (249) appear to have a direct bearing on the study of clays. According to him, the extent of ionization of the colloidal micelle plays a dominant role in bringing about variations in viscosity, since increase in ionization resulted in the release of more hydrophilic ends in the clay systems. The investigations of Marshall (230), Wiegner (74), Baver (250),Kruyt (247) and others on the ionization of the exchangeable cations, also support this view point.

Hydration effects on viscosity:

A number of workers have tried to explain the viscosity variations of clays,in terms of hydration, inspite of their large dependence on charge and zeta potential for their stability. Highly hydrated ions draw water into the particle, producing swelling and therefore, an increase in viscosity. Baver (250), on the other hand, considers hydration in terms of the formation of a water film around the particles, due to the adsorption of highly hydrated ions, or to water held between the particles in aggregate formation. Two forces exert influence on viscosity:

dispersion tends towards a decrease in viscosity,while hydration causes an increase in viscosity. Furthermore, as the concentration of foreign ions in the solution increases beyond a certain limit, the property of hydration decreases, with consequent reduction in viscosity.

Viscosity and the lyotropic series of ions:

Excellent co-relation between the lyotropic series and viscosity variations is said to exist in most of the colloidal systems. Loeb (251) had differed from such a generalization, particularly when dealing with protein suspensions. According to him, viscosity changes can also occur due to lack of control of H^+ ion concentration. Although such influences are understandable in colloids prone to pH variations, it is difficult to say whether this can also happen in case of clays. Bradfield (252) had indicated some such probability, on the basis of this experiment on the flocculation of clay suspensions,where he found that flocculation values not only change with concentration of the sol, kind of clay minerals and the nature of exchangeable ions, but also vary widely with slight changes in hydrogen ion concentration. More or less similar conclusions were arrived at by Wiegner (74),Baver (250), Mattson (253), Kelley (75), and Jenny (73), while investigating the stability of clay suspensions.

Clay suspensions are easily flocculated,by the addition of small amounts of neutral salts. Schulze-Hardy rule is only approximately followed, since the minimum electrolyte requirement varies with the pH, the nature of the adsorbed cation and the concentration of the sol, (74,254). Unlike hydrophobic colloidal solutions,a decrease in the thickness of the double layer is not a direct consequence of added electrolyte but takes place through ionic exchange. Interesting results are obtained, when flocculation of clays having hydrated ions, is carried out by adding ions of similar type.

Modes of particle association:

When a suspension of plate like clay particles flocculates, three different modes of particle association may occur; face to face (FF), edge to face (EF) and edge to edge (EE). The electrical interaction energy will be different for the three types of associations and is governed by three different combinations of the two double layers. Moreover, the van der Waals interaction energy will also be different for the three types of association, since a different geometry must be considered in the summation of the attraction between all the atom pairs of the approaching plates,(255). Consequently, the three types of association will not necessarily occur simultaneously, or to the same extent, when a clay suspension is flocculated.

Viscosity of dilute clay suspensions increases, when conglomerates are formed by EE and EF association; the viscosity decreases when the particles become thicker by FF association. In concentrated clay suspensions EE and EF association leads to the formation of continuous, linked, card house structures, which extend throughout the total available volume, giving rise to gels, which are characterized by a Bingham yield stress. If FF association occurs simultaneously, the number of units building the card house structure is reduced.

Influence of electrolytes on the viscosity of clay suspensions:

In presence of a few m.e.q. of NaCl, in a Na-montmorillonite suspension, both double layers are compressed and their effective charge is reduced. Consequently, both EF attraction and FF repulsion diminish and the viscosity decreases. When the amount of NaCl in the suspension is increased, the thickness of the both double layer is decreased. The van der Waals attraction between EF then becomes operative and the particles are either without charge, or possess only a small residual charge, and once again the conditions become favourable for the formation of card house structure. At very high salt concentrations yield stress or the viscosity decreases, due to the simultaneous FF attraction, by which the number of particles in the card house is reduced.

Sodium montmorillonite is exceptional in its behaviour with changing salt concentrations. For other clays the various features of the salt effect curves are often less pronounced, or even absent, because of the domination of one type of association in a wide salt concentration region, e.g., a sodium kaolinite does not show increase in viscosity after the pure gel is broken down, by the addition of the small amount of salt. In other clays e.g., calcium montmorillonite the initial sharp decrease in the viscosity does not occur.

Apparently different clays react differently on electrolyte addition, because of differences in their double layer structures.

Inspite of the fact, that large amount of work has been done on the viscosity of clay suspensions and valuable data accumulated therein, nothing precise has been said till now, regarding the role of ions of the so called Hofmeister series visa vis hydrogen ion concentration. Recently Singhal and Malik (127) have done work in this direction using bentonite from different places. It was, therefore, thought worthwhile to apply their approach regarding the effect of pH and Hofmeister series of ions to these transformed clay structures.

Characterization of clay minerals from viscosity measurements:

Identification of clay minerals, with the help of viscosity measurements, in soil and clay samples, has attracted the attention of quite a few workers. Amongst those who have made notable contribution, mention may be made of Mattson (256) and Baver (257) who gave a possible inter relationship between the viscosity of clays and the amount and nature of adsorbed cations, by carrying out viscosity titrations of H-bentonite and beidellite respectively, with alkali metal hydroxides and got smooth curves, (on plotting volume of alkali against viscosity), with alternate maxima and minima. Similar observations were made by Mukherjee (203) with Indian bentonite samples. Investigations on clays other than bentonites, were carried out by Mukherjee (113), Chakravarti (258), Adhikari (193), Marshall (259) and others, who observed that Kaolinite, when titrated against monovalent alkalies, showed an initial fall in viscosity, followed by a constancy in the viscosity values, while a similar constancy preceded by a not well pronounced maxima was observed by them in case of H-illite.

Mukherjee and Mitra (113,191) have summarized, that on the gradual addition of the alkali to hydrogen bentonites, their viscosity increases and passes through a maximum value, at a point corresponding to about 75% neutralization, of the amount of the acid given by the inflection point of the titration curve. Apart from a slight initial decrease, the alkali has no marked effect on the viscosity of hydrogen kaolinite.

Chakravarti (258) has concluded that by virtue of its higher zeta potential and hydration, hydrogen montmorillonite clay suspension behaves as a hydrophilic colloid, whereas H-kaolinite possessing a lower zeta potential and low hydration behaves as a hydrophobic colloid. The viscosity of hydrogen kaolinite increases regularly but slightly and that of H- montmorillonite increases more or less rapidly with increasing concentration of the suspension.

From the purely physical point of view, bentonite or a clay containing montmorillonite should behave differently from kaolin and illite as far as their colloidal properties are concerned. It should also hold good for soils containing these minerals in varying proportions. In a very similar fashion a mixture of montmorillonite with a metal hydroxide can be differentiated from a complex of montmorillonite-metal hydroxide or even an interstratified crystal of the two or also from other clay minerals. Influence of the Hofmeister series of ions and pH on the viscosity of these transformed bentonite structures (chlorites) should form the basis of interesting study, both from the fundamental and applied view point.

EXPERIMENTAL

Preparation of clay sols:

The powdered clay samples were treated with 0.02 N HCl, in order to remove the free metal hydroxide and also to convert the clay in the hydrogen form. Utmost care was used in this treatment, so as to avoid any structural decomposition of the clay, tested by the dissolution of alumina or silica in the leachate. The clay was afterwards washed thoroughly with 1:1 alcohol-water mixture and dried in the oven. It was then dispersed in double distilled water, by stirring in the mechanical shaker for two hours, followed by centrifugation at 3000 r.p.m. for half an hour. The clear sol thus obtained was passed through a generated column of H-form of Amberlite IR -120 to remove the last traces of any free metal hydroxide.

Charge determination:

The migration of colloidal particles, under the influence of an applied e.m.f., was determined by electrophoresis apparatus(Burton Type). The sols of the various clays were placed in the lower part of the U-tube and were carefully covered by the dispersion medium i.e., water, in which dipped platinum electrodes connected to a source of e.m.f.. The boundary of the sols in each case (of all the clay samples) started to move towards the positive electrode, indicating that clay sols consisted of negatively charged particles.

Preparation of standard solutions:

Standard solutions of various electrolytes(NaOH, KOH, $Ca(OH)_2$, NaCl, NaI, NaCNS,$NaNO_3$,$NaClO_3$,Na_2SO_4 , $NaCH_3$ COO and sodium citrate) were prepared by the usual methods.

pH measurements:

The pH of the clay sols were measured with a Cambridge Bench Type pH meter with glass colomel electrode assembly.

Viscosity measurements:

Viscosity measurements were made at a constant temperature of $30 \pm 0.01^{\circ}C$ and pressure of 30 cms.of water. The method used for viscosity measurement was the one devised by Scarpa (260) and modified by Farrow (261) and later by Joshi (262).

The apparatus consisted of three parts,(a) viscometers,(b) apparatus for generating and maintaining low constant pressure,(c) thermostatic water bath. Ostwald's viscometers B.S.S. type No.2 were used for these determinations. A number of viscometers were used simultaneously to facilitate a larger number of determinations within a short time interval. The viscometers were connected through pressure rubber tubings to the source of reduced pressure. Viscometers were well cleaned with NaOH and chromic acid solutions, washed with distilled water, alcohol and then dried by air blower before use in each case.

Second part of the apparatus consisted of two large aspirator bottles interconnected to each other with pressure rubber tubings so that any diminuation of pressure in one caused a simultaneous and equivalent reduction in the other and could be read off by a manometer. Manometer consisted of a clean glass U-tube of suitable dimensions fixed along a scale to read the pressure. Coloured water was used in the manometer. Reduction of pressure could be affected by means of a suction pump connected to the first aspirator and was carefully regulated. Second aspirator was connected to two glass tubes mounted over a stand each carrying a system of stoppers. Vacuum could be applied to the viscometer, by proper adjustments of these stoppers, which caused a rise in the liquid placed in the viscometer. Access to air could be provided either to the viscometer or the aspirator bottles by opening suitable stoppers.

The temperature of the thermostatic water-bath was regulated by means of a mercury-toluene regulator, which worked through an electromagnetic relay to an accuracy of $\pm 0.01^{\circ}C$. Sufficient time was allowed for the viscometer to attain the temperature of the bath,before actual measurements were carried out. Using this method the viscosity η_s of a liquid could be determined by the formula

$$\eta_s = K \frac{t_1 t_2}{t_1 + t_2}$$

where t_1 and t_2 are the times for rise and fall of the liquid, under a constant pressure and temperature and K is the viscometer constant. The values of the constants of the viscometers used in these measurements were obtained by determining t_1 and t_2 for a standard substance such as double distilled water under a constant pressure and temperature. Greatest precaution was taken to regulate the pressure, so that it remained constant in each determination. The procedure employed for determining the viscosities was as follow~~ed~~s:

A constant volume of the substance under examination was taken in the viscometer, which was then fitted to a stand, immersed in the constant temperature bath and connected to the source of low pressure. After a definite interval of time readings were taken by opening the proper stoppers. The time of rise from the lower mark to the upper mark in the bulb of the capillary limb of the viscometers was noted with a stop watch, reading upto 1/10 th of a second. This gave t_1 . The stopper for making access to air for the viscometer was now opened,closing the former stopper and the liquid now started to fall under gravity. The time of fall from the upper to the lower mark was now noted. This gave t_2 . Knowing the constant for the viscometer and the time of rise and fall of the liquid, the viscosity for the given suspension was calculated.

Following sets of experiments were performed: (a) determination of the viscometer constant,(b) observations for changes in $\eta_s - \eta_m / \eta_m$ (where η_m is the viscosity of the dispersion medium) in presence of varying amounts of alkalies,(c) variations in $\eta_s - \eta_m / \eta_m$ with changes in pH in presence of a fixed amount of electrolyte.

SET ONE

Variations in $n_s - n_m / n_m$ of clay sols in presence of varying amounts of alkalies:

To 10.0 ml. of the clay sol, prepared as described earlier,(which was, then, equilibrated to a pH of 7.0 by the addition of the required amount of NaOH), was added different concentrations of the alkali and the volume was made constant to 11.0 ml. in each case, by adding double distilled water, to avoid the dilution effect. The mixture was filled into the viscometer upto the given mark, placed in the thermostat and the viscosity recorded 30 mts.after addition of electrolyte. Results are given in the tables below.

Viscometer constant:

A number of viscometers were used even in the same set of readings. The values of the different viscometer constants (K), used in the case of bentonite clay sols, were the same and equal to 0.1272. Similarly all the other viscometers, used in the case of remaining clay sols, gave the same constant K values equal to 0.03498.

RESULTS

TABLE No.1.

Bentonite clay sol.

m.e.q. of alkali per 100 gm. clay.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
(a). Readings with NaOH.				
0.0	14.5	24.3	1.182	0.4761
5.0	14.7	27.0	1.203	0.5023
10.0	14.9	25.6	1.226	0.5311
20.0	15.6	28.0	1.275	0.5920
30.0	16.0	28.5	1.303	0.6273
40.0	16.6	29.7	1.355	0.6929
50.0	16.9	30.2	1.379	0.7221
Fig.1 a, Curve 1.				
(b). Readings with KOH.				
0.0	14.5	24.3	1.182	0.4761
5.0	14.8	26.9	1.215	0.5175
10.0	14.9	25.6	1.226	0.5311
20.0	16.0	28.5	1.303	0.6273
30.0	16.3	29.4	1.335	0.6675
40.0	16.9	30.2	1.379	0.7221
50.0	17.2	32.0	1.423	0.7772
Fig.1 a, Curve 2.				
(c). Readings with $Ca(OH)_2$				
0.0	14.5	24.3	1.182	0.4761
5.0	14.9	25.6	1.226	0.5311
10.0	15.3	22.1	1.255	0.5672
20.0	16.0	28.5	1.303	0.6273
30.0	16.6	29.7	1.355	0.6929
40.0	17.0	30.9	1.395	0.7423
50.0	17.5	32.0	1.439	0.7970
Fig.1 a, Curve 3.				

TABLE No. 2.

Magnesium chlorite
clay sol.

m.e.q. of alkali per 100 gm. clay.	Time of rise. seconds.	Time of fall. seconds.	η_s centipoise.	$\eta_s - \eta_m / \eta_m$
(a). Readings with NaOH.				
0.0	52.5	110.5	1.2487	0.560
5.0	52.8	119.2	1.2967	0.620
10.0	53.2	131.0	1.3263	0.657
20.0	53.4	145.0	1.3687	0.710
30.0	53.7	152.5	1.4015	0.751
40.0	54.2	162.0	1.4239	0.779
50.0	54.4	159.0	1.4303	0.787
Fig.2 a, Curve 1.				
(b). Readings with KOH.				
0.0	52.5	110.5	1.2487	0.560
5.0	52.9	126.1	1.3042	0.629
10.0	53.5	136.7	1.3445	0.679
20.0	53.8	149.5	1.3846	0.728
30.0	54.0	161.5	1.4163	0.769
40.0	54.2	170.2	1.4359	0.793
50.0	54.4	172.8	1.4483	0.809
Fig.2 a, Curve 2.				
(c). Readings with $Ca(OH)_2$				
0.0	52.5	110.5	1.2487	0.560
5.0	53.5	116.6	1.2827	0.640
10.0	54.3	134.0	1.3525	0.689
20.0	55.2	146.2	1.4015	0.750
30.0	55.7	151.8	1.4263	0.781
40.0	55.9	157.0	1.4427	0.801
50.0	60.2	134.1	1.4538	0.815

Fig. 2 a, Curve 3.

VISCOSITY VARIATIONS WITH ALKALI CONCN.
IN (a) Mg-CHLORITE & (b) Ni-CHLORITE

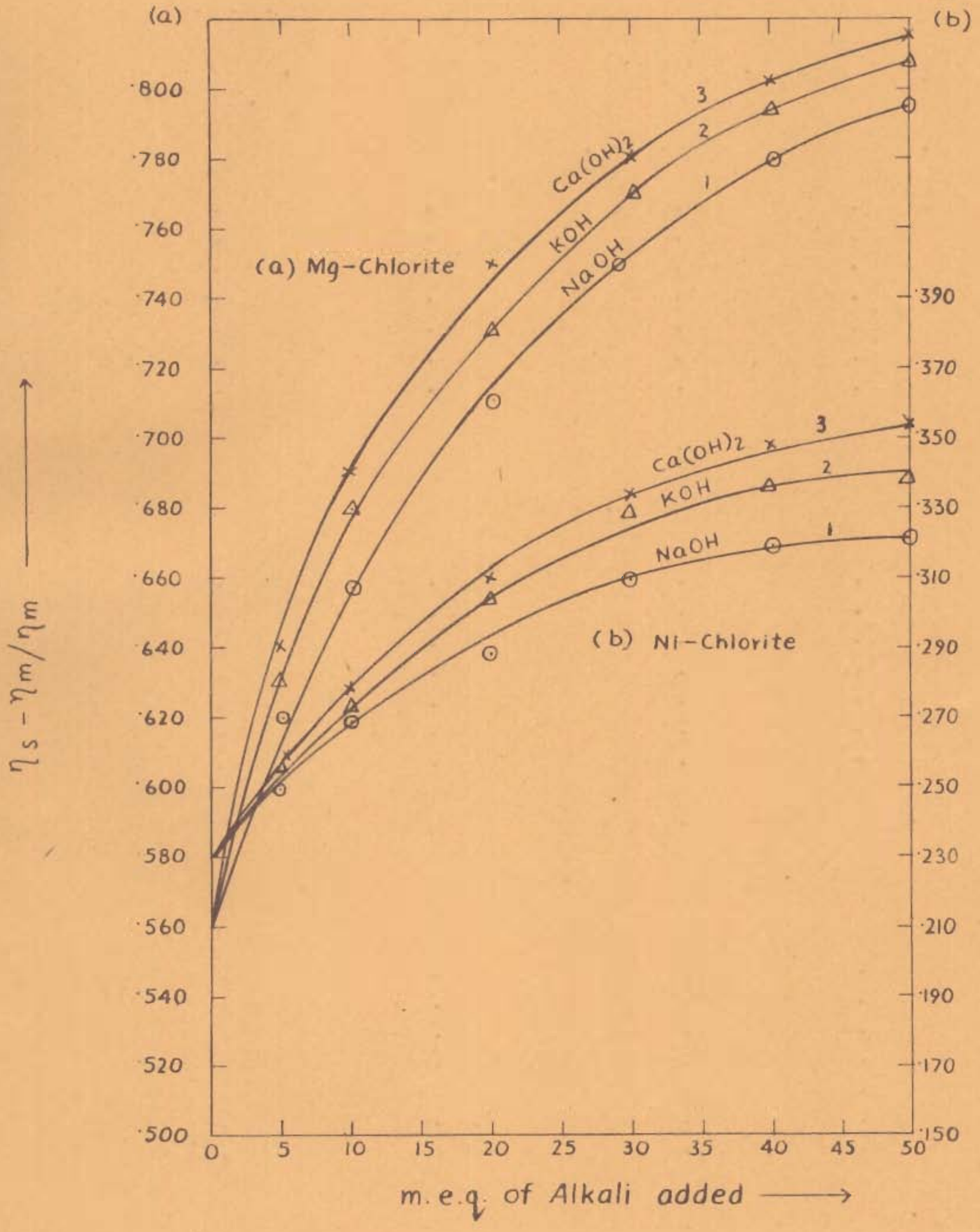


FIG. 2

TABLE No. 3.

Nickel chlorite
clay sol.

m.e.q. of alkali per 100 gm. clay.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
		(a). Readings with NaOH.		
0.0	46.5	71.8	0.9848	0.231
5.0	46.6	73.8	0.9999	0.249
10.0	46.7	77.0	1.0167	0.270
20.0	46.8	80.0	1.0311	0.288
30.0	46.9	83.0	1.0479	0.309
40.0	47.0	84.6	1.0551	0.318
50.0	47.1	85.0	1.0583	0.322

Fig.2 b, Curve 1.

(b). Readings with KOH.

0.0	46.5	71.8	0.9848	0.231
5.0	46.8	74.4	1.0047	0.253
10.0	47.0	77.1	1.0209	0.273
20.0	47.2	81.3	1.0435	0.302
30.0	47.3	83.4	1.0557	0.318
40.0	47.5	85.2	1.0683	0.335
50.0	47.6	85.4	1.0692	0.338

Fig. 2 b, Curve 2.

(c). Readings with $Ca(OH)_2$.

0.0	46.5	71.8	0.9848	0.231
5.0	47.2	73.4	1.0055	0.256
10.0	47.5	74.4	1.0133	0.277
20.0	48.3	79.5	1.0494	0.310
30.0	48.7	81.3	1.0683	0.333
40.0	49.2	83.5	1.0796	0.348
50.0	50.0	82.1	1.0842	0.354

Fig. 2 b, Curve 3.

TABLE No.4.

Ferric chlorite
clay sol.

m.e.q. of alkali per 100 gm. clay.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$

(a). Readings with NaOH.

m.e.q. of alkali per 100 gm. clay.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
0.0	47.2	87.5	1.0719	0.339
5.0	47.5	122.5	1.1239	0.404
10.0	47.9	109.4	1.1655	0.456
20.0	48.2	124.0	1.2159	0.519
30.0	48.3	136.6	1.2487	0.561
40.0	48.5	141.4	1.2631	0.578
50.0	48.7	142.5	1.2703	0.587

Fig. 5 a, Curve 1.

(b). Readings with KOH.

0.0	47.2	87.5	1.0719	0.339
5.0	47.9	100.7	1.1372	0.420
10.0	48.2	110.3	1.1729	0.465
20.0	48.5	129.2	1.2355	0.543
30.0	48.6	136.0	1.2533	0.565
40.0	48.9	140.8	1.2700	0.586
50.0	49.0	144.1	1.2791	0.597

Fig. 5 a, Curve 2.

(c). Readings with $Ca(OH)_2$.

0.0	47.2	87.5	1.0719	0.339
5.0	47.7	107.0	1.1537	0.441
10.0	48.3	118.4	1.2010	0.499
20.0	48.5	135.2	1.2493	0.560
30.0	48.7	139.3	1.2613	0.575
40.0	48.9	141.6	1.2787	0.596
50.0	49.0	146.1	1.2834	0.602

Fig. 5 a, Curve 3.

VISCOSITY VARIATIONS WITH ALKALI CONCN.
IN
(a) FERRIC CHLORITE (b) ALUMINIUM CHLORITE

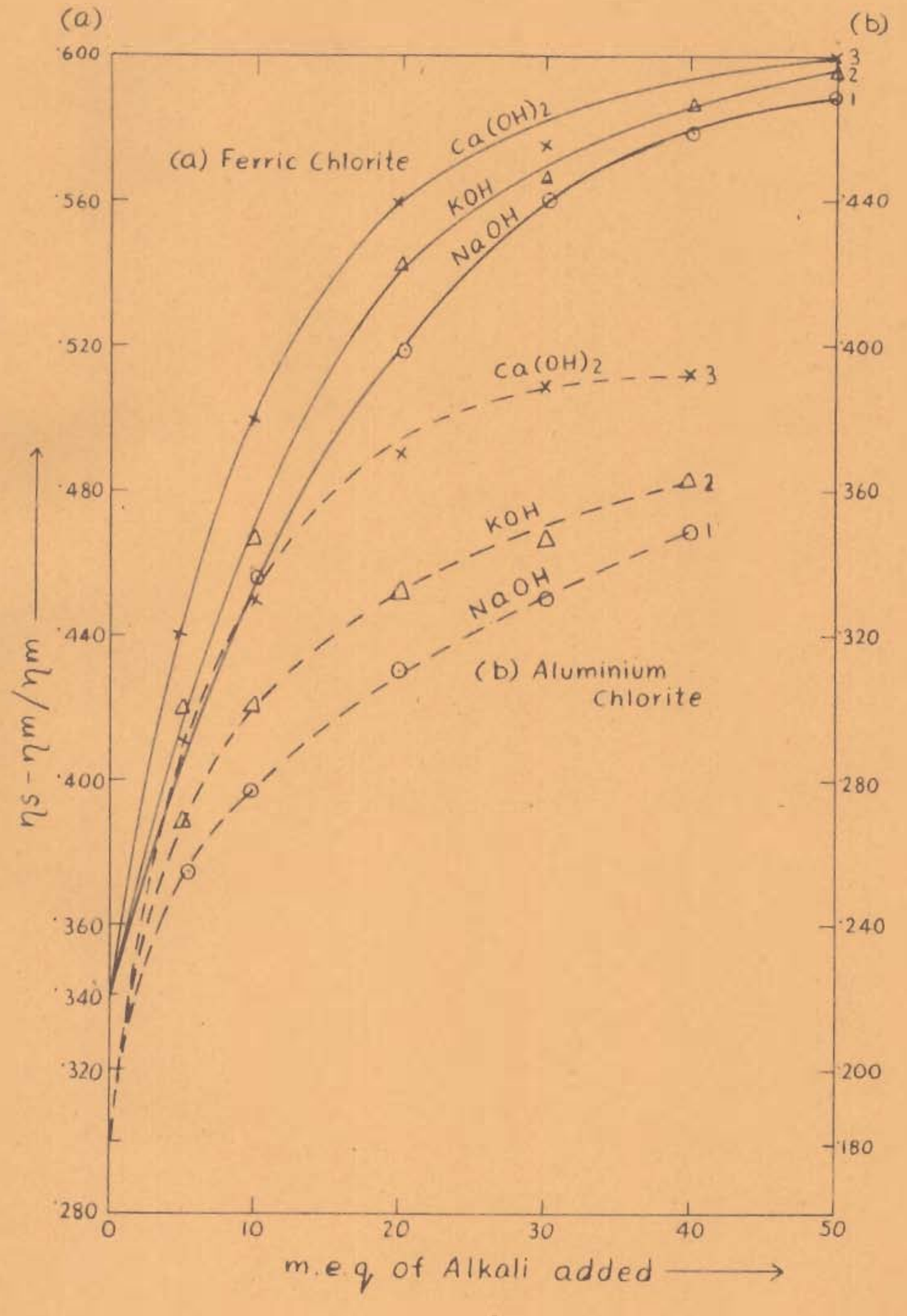


FIG. 5

TABLE No.5.

Aluminum chlorite
clay sol.

m.e.q. of alkali per 100 gm. clay.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m$ / η_m
		(a). Readings with NaOH.		
0.0	43.6	78.5	0.9455	0.180
5.0	43.9	83.6	1.0045	0.254
10.0	44.3	87.3	1.0222	0.276
20.0	44.6	93.5	1.0493	0.310
30.0	44.8	95.6	1.0656	0.331
40.0	44.9	98.9	1.0799	0.348
		Fig.5b, Curve 1.		
		(b). Readings with KOH.		
0.0	43.6	78.5	0.9455	0.180
5.0	43.9	86.1	1.0151	0.268
10.0	44.8	89.0	1.0407	0.300
20.0	45.3	94.0	1.0657	0.331
30.0	45.5	94.6	1.0772	0.345
40.0	45.8	98.5	1.0922	0.363
		Fig.5b, Curve 2.		
		(c). Readings with $Ca(OH)_2$.		
0.0	43.6	78.5	0.9455	0.180
5.0	43.7	94.2	1.0347	0.291
10.0	43.9	97.8	1.0563	0.319
20.0	44.2	109.0	1.0963	0.369
30.0	44.4	113.0	1.1130	0.388
40.0	44.5	113.0	1.1162	0.393
		Fig.5b, Curve 3.		

SET TWO

Variations in $\eta_s - \eta_m / \eta_m$ of the clay sols with change in pH in presence of fixed amount of electrolytes:

Ten ml. of the clay sol was mixed with varying amounts of N/10 NaOH and 0.10 ml. of N/10 electrolyte in each case. The dilution effect was avoided by adding double distilled water to the mixture and making up the volume same (12.0 ml.) in every case. The required volume of the mixture was transferred to the viscometer, which was then placed in the thermostat. Readings for viscosity were taken after keeping the sol-alkali-electrolyte mixture for six hours. Results obtained are recorded in the following tables.

TABLE No. 1.

Bentonite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	pH	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
		(a). Readings with NaCl.			
1.	15.0	24.5	3.07	1.183	0.4774
2.	14.0	22.3	3.32	1.094	0.3663
3.	12.9	21.2	3.74	1.020	0.2738
4.	12.5	20.6	4.50	0.989	0.2360
5.	12.4	20.4	5.00	0.972	0.2139
6.	12.4	20.4	6.28	0.972	0.2139
7.	12.4	20.4	8.12	0.972	0.2139
		(Fig.1 b,Curve 1).			
		(b). Readings with NaI.			
1.	14.9	25.6	3.02	1.226	0.5311
2.	14.0	22.5	3.45	1.098	0.3713
3.	12.9	21.2	4.11	1.020	0.2738
4.	12.5	20.8	4.42	0.993	0.2408
5.	12.4	20.5	5.30	0.972	0.2139
6.	12.4	20.5	6.72	0.972	0.2139
7.	12.4	20.5	8.69	0.972	0.2139
		(Fig. 1 b,Curve 2).			
		(c). Readings with Sodium citrate.			
1.	14.5	24.3	2.92	1.182	0.4761
2.	13.5	22.5	3.85	1.078	0.3463
3.	13.0	21.5	5.80	1.030	0.2863
4.	12.6	21.2	6.75	1.005	0.2551
5.	12.5	20.6	8.85	0.989	0.2360
6.	12.4	20.0	10.00	0.974	0.2172
		(Fig. 1 b, Curve 3).			

(a) VISCOSITY VARIATIONS WITH ALKALI CONCN IN BENTONITE

(b) VISCOSITY VARIATIONS WITH pH IN BENTONITE IN PRESENCE OF FIXED AMOUNT OF ANIONS

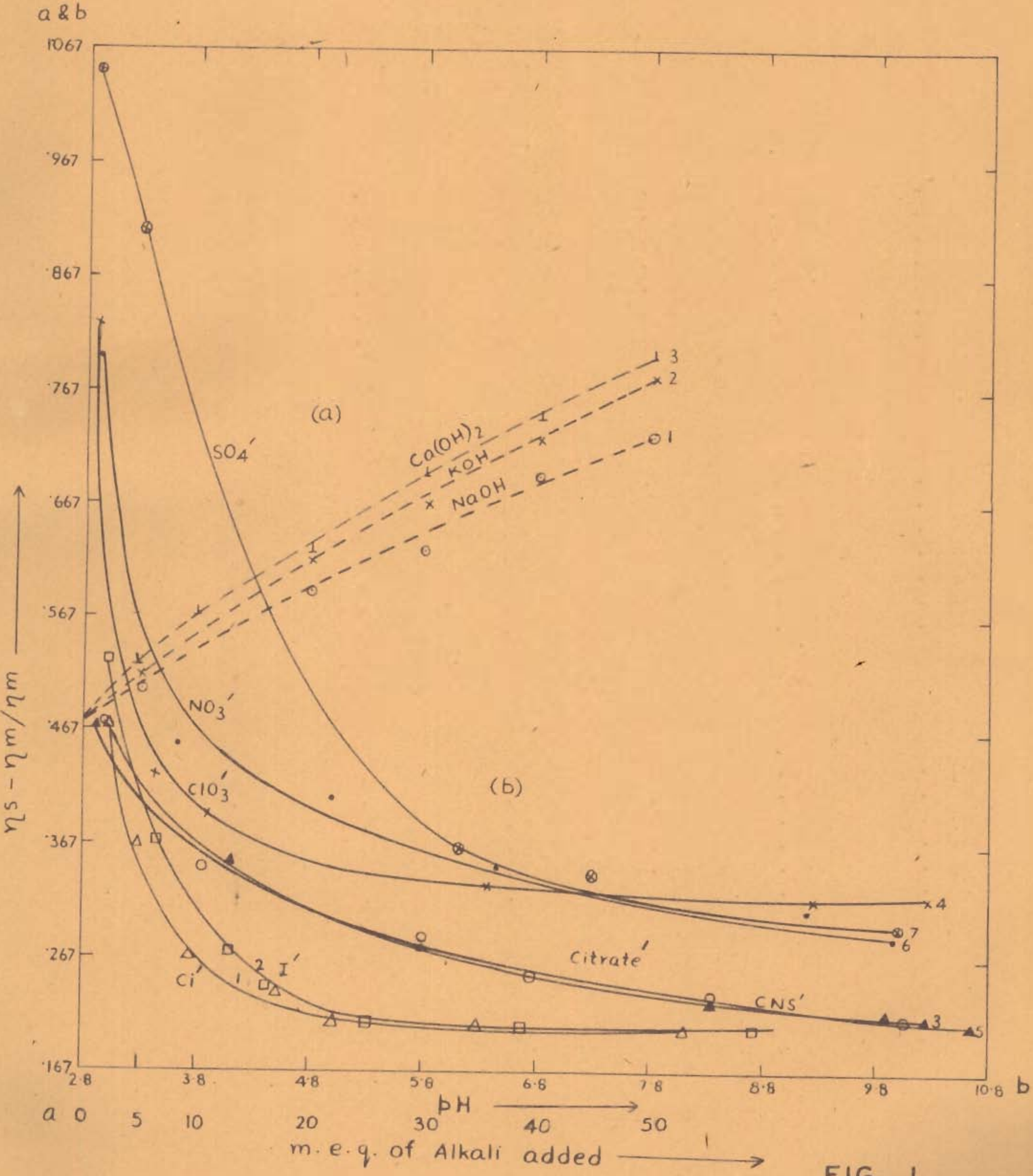


FIG. 1

TABLE No. 1.

Bentonite clay sol.

(d). Readings with $NaClO_3$.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	pH	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
1.	17.7	32.7	2.91	1.463	0.8271
2.	14.2	24.5	3.46	1.144	0.4288
3.	14.0	23.6	3.85	1.118	0.3963
4.	13.5	22.1	6.36	1.066	0.3313
5.	13.4	22.0	9.25	1.059	0.3225
6.	13.4	22.0	10.25	1.059	0.3225

(Fig. 1 b, Curve 4).

(e). Readings with NaCNS.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	pH	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
1.	14.5	24.3	2.85	1.182	0.4761
2.	13.8	22.1	4.10	1.081	0.3501
3.	13.0	21.5	5.80	1.030	0.2863
4.	12.5	20.6	8.35	0.9897	0.2360
5.	12.5	20.1	9.86	0.9804	0.2244
6.	12.4	20.0	10.22	0.9746	0.2172
7.	12.3	19.8	10.64	0.9651	0.2053

(Fig. 1 b, Curve 5).

(f). Readings with $NaNO_3$.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	pH	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
1.	17.5	32.0	2.93	1.439	0.7970
2.	14.5	24.7	3.66	1.162	0.4512
3.	14.0	24.0	5.11	1.125	0.4059
4.	13.5	22.5	6.47	1.078	0.3463
5.	13.2	22.1	9.20	1.051	0.3135
6.	12.9	21.5	9.98	1.025	0.2800

(Fig. 1 b, Curve 6).

TABLE No. 1.

Bentonite clay sol.

Sl. No.	Time of rise. seconds.	Time of fall. seconds.	pH	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$
(g). Readings with Na_2SO_4 .					
1.	19.2	39.0	2.87	1.637	1.044
2.	18.0	36.0	3.31	1.527	0.9080
3.	16.0	28.5	4.48	1.303	0.6273
4.	13.7	23.0	6.09	1.092	0.3637
5.	13.5	22.5	7.30	1.078	0.3463
6.	13.0	21.8	10.00	1.035	0.2926

(Fig. 1 b, Curve 7).

TABLE No. 2.

Magnesium chlorite
clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
(a). Readings with Sodium citrate.					
1.	56.2	143.5	1.4071	0.758	4.00
2.	55.9	134.0	1.3735	0.716	4.53
3.	55.7	133.5	1.3695	0.711	5.05
4.	55.6	132.8	1.3647	0.705	6.00
5.	55.7	135.8	1.3767	0.720	7.00
6.	55.9	171.4	1.4671	0.833	8.05
7.	57.3	237.0	1.6071	1.008	9.07
(Fig. 3, Curve 1).					
(b). Readings with Na_2SO_4 .					
1.	58.0	129.1	1.4010	0.749	4.00
2.	57.3	125.5	1.3730	0.715	4.50
3.	57.0	124.0	1.3612	0.700	5.02
4.	55.7	126.2	1.3464	0.682	6.00
5.	56.2	129.0	1.3633	0.702	7.00
6.	59.9	132.0	1.4398	0.799	8.02
7.	61.4	168.1	1.5692	0.960	9.05
(Fig. 3, Curve 2).					
(c). Readings with Sodium acetate.					
1.	57.4	129.5	1.3931	0.740	4.00
2.	57.0	125.0	1.3662	0.706	4.52
3.	55.9	127.0	1.3540	0.691	5.03
4.	54.7	127.7	1.3359	0.668	6.00
5.	55.2	128.7	1.3439	0.679	7.01
6.	58.2	130.8	1.4089	0.760	7.97
7.	59.9	151.2	1.4998	0.873	9.00
(Fig. 3, Curve 3).					
(d). Readings with NaCl.					
1.	56.7	131.2	1.3839	0.729	4.01
2.	56.5	126.2	1.3612	0.700	4.54
3.	56.3	121.8	1.3442	0.679	5.03
4.	56.0	116.7	1.3215	0.650	5.98
5.	56.3	118.1	1.3283	0.659	6.95
6.	59.2	122.8	1.3964	0.744	8.04
7.	60.5	138.2	1.4675	0.832	8.90
(Fig.3, Curve 4).					

Table contd..

VISCOSITY VARIATIONS WITH pH IN Mg-CHLORITE IN PRESENCE OF FIXED AMOUNT OF ANIONS

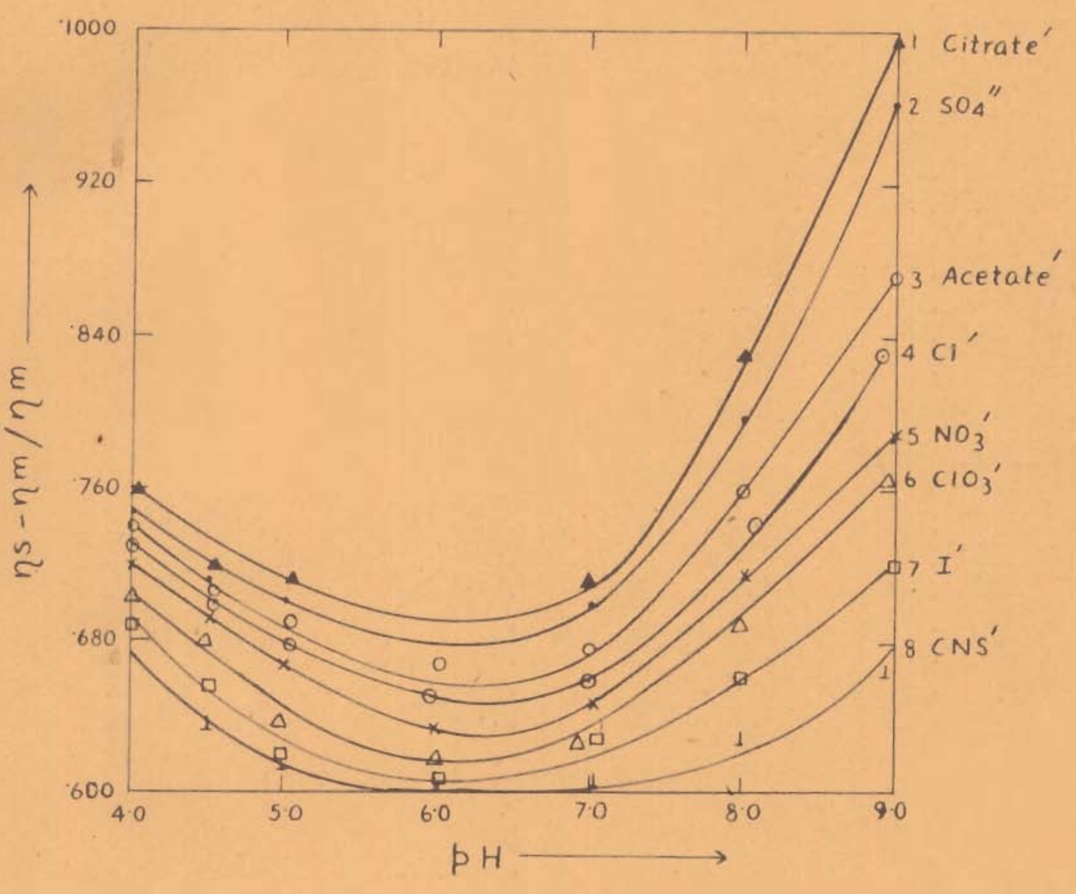


FIG · 3

TABLE No. 2.

Magnesium chlorite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
		(e). Readings with $NaNO_3$.			
1.	59.1	191.0	1.5759	0.719	4.02
2.	55.4	130.3	1.3547	0.692	4.47
3.	55.1	126.1	1.3351	0.667	5.01
4.	54.5	119.4	1.3082	0.633	5.98
5.	52.3	139.5	1.3260	0.645	6.99
6.	56.6	129.2	1.3761	0.718	8.04
7.	57.3	146.1	1.4362	0.793	9.01
		(Fig.3, Curve 5).			
		(f). Readings with $NaClO_3$.			
1.	55.9	131.0	1.3624	0.702	4.01
2.	55.5	126.0	1.3438	0.679	4.47
3.	55.3	118.6	1.3112	0.638	4.98
4.	55.0	114.3	1.2950	0.619	6.00
5.	55.1	116.5	1.3045	0.630	6.95
6.	56.0	125.0	1.3508	0.687	7.97
7.	57.0	140.5	1.4157	0.768	8.97
		(Fig.3, Curve 6).			
		(g). Readings with NaI.			
1.	55.6	196.3	1.3551	0.693	4.01
2.	55.4	121.5	1.3255	0.656	4.51
3.	55.1	116.6	1.3015	0.626	5.01
4.	54.9	112.0	1.2879	0.609	6.02
5.	54.9	116.1	1.2951	0.618	7.02
6.	55.3	122.0	1.3279	0.659	8.02
7.	55.9	137.6	1.3806	0.725	9.00
		(Fig. 3, Curve 7).			
		(h). Readings with NaCNS.			
1.	55.6	123.6	1.3372	0.671	4.00
2.	55.2	117.2	1.3065	0.632	4.50
3.	54.9	116.0	1.2934	0.616	5.00
4.	54.7	111.2	1.2816	0.601	6.00
5.	54.8	111.1	1.2848	0.605	7.05
6.	55.1	116.9	1.3038	0.629	8.00
7.	55.3	118.9	1.3139	0.664	8.95
		(Fig. 3, Curve 8).			

TABLE No. 3.

Nickel chlorite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
		(a). Readings with Sodium citrate.			
1.	48.0	85.1	1.0737	0.3410	4.00
2.	48.3	93.2	1.1129	0.3900	4.70
3.	48.4	97.8	1.1325	0.4140	5.45
4.	48.5	99.4	1.1399	0.4240	6.50
5.	48.4	99.4	1.1389	0.4220	7.25
6.	48.3	97.4	1.1293	0.4100	8.00
7.	48.1	93.6	1.1112	0.3870	9.00
		(Fig. 4, Curve 1).			
		(b). Readings with Na_2SO_4 .			
1.	48.5	80.5	1.0563	0.3192	4.00
2.	48.8	91.6	1.1012	0.3749	4.65
3.	48.9	93.7	1.1237	0.4037	5.45
4.	50.0	93.0	1.1363	0.4198	6.45
5.	50.2	92.9	1.1352	0.4183	7.25
6.	50.1	91.5	1.1303	0.4120	8.02
7.	50.0	89.8	1.1200	0.3971	9.00
		(Fig.4, Curve 2).			
		(c). Readings with Sodium acetate.			
1.	47.5	81.0	1.0478	0.3085	4.00
2.	47.7	89.8	1.0893	0.3602	4.75
3.	47.9	93.2	1.1076	0.3837	5.50
4.	48.3	95.9	1.1235	0.4035	6.55
5.	48.4	95.7	1.1253	0.4050	7.27
6.	48.1	94.2	1.1172	0.3957	8.05
7.	48.0	92.5	1.1059	0.3810	9.00
		(Fig. 4, Curve 3).			
		(d). Readings with NaCl.			
1.	47.9	78.3	1.0399	0.2980	4.00
2.	48.3	84.6	1.0759	0.3439	4.75
3.	48.5	90.0	1.1039	0.3782	5.45
4.	48.8	91.7	1.1160	0.3930	6.47
5.	48.7	92.0	1.1139	0.3910	7.25
6.	48.5	91.1	1.1078	0.3840	8.00
7.	48.4	85.1	1.0790	0.3480	8.95
		(Fig.4, Curve 4).			

VISCOSITY VARIATIONS WITH pH IN Ni-CHLORITE IN PRESENCE OF FIXED AMOUNT OF ANIONS

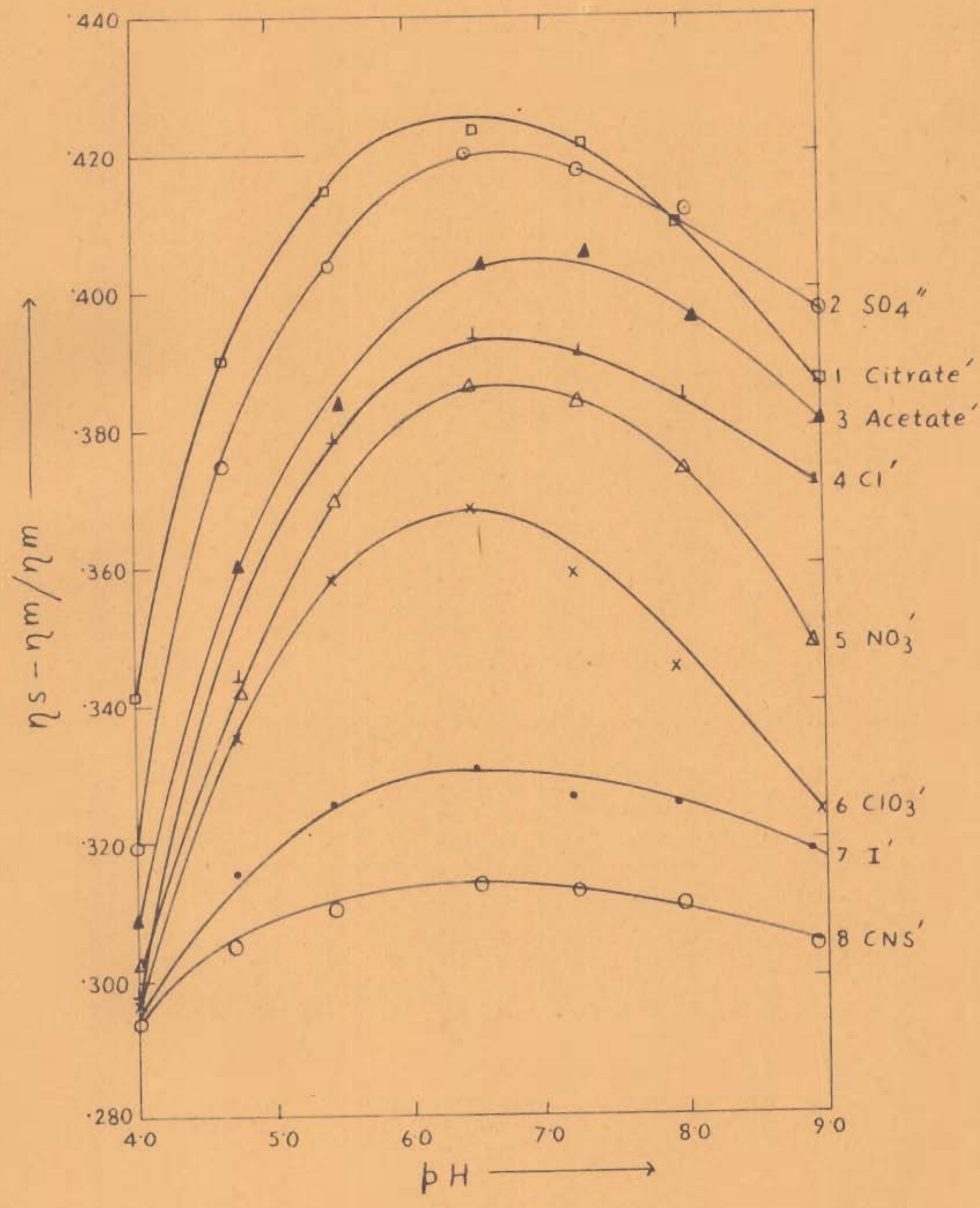


FIG. 4

TABLE No. 3.

Nickel chlorite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
		(e). Readings with $NaNO_3$.			
1.	48.3	78.0	1.0433	0.3025	4.00
2.	48.7	83.4	1.0747	0.3418	4.75
3.	49.1	88.7	1.1059	0.3695	5.43
4.	49.3	89.0	1.1095	0.3864	6.44
5.	49.2	88.9	1.1071	0.3837	7.23
6.	49.0	88.2	1.1007	0.3740	8.00
7.	48.8	83.7	1.0799	0.3482	8.95
		(Fig.4, Curve 5).			
		(f). Readings with $NaClO_3$.			
1.	47.6	79.4	1.0379	0.2960	4.00
2.	48.2	84.0	1.0685	0.3347	4.75
3.	48.5	87.2	1.0880	0.3581	5.45
4.	48.7	88.0	1.0965	0.3680	6.45
5.	48.6	90.9	1.0883	0.3592	7.20
6.	48.5	84.5	1.0760	0.3453	7.95
7.	48.3	82.0	1.0609	0.3250	9.00
		(Fig.4, Curve 6).			
		(g). Readings with NaI.			
1.	48.8	75.6	1.0370	0.2950	4.00
2.	49.2	78.5	1.0532	0.3153	4.75
3.	49.2	79.0	1.0557	0.3252	5.45
4.	49.4	79.8	1.0647	0.3304	6.50
5.	49.3	79.6	1.0620	0.3265	7.18
6.	49.2	79.8	1.0610	0.3250	7.95
7.	49.0	79.2	1.0557	0.3188	8.95
		(Fig.4, Curve 7).			
		(h). Readings with NaCNS.			
1.	47.5	71.5	0.9963	0.2940	4.00
2.	48.6	78.0	1.0448	0.3055	4.73
3.	48.7	78.0	1.0495	0.3110	5.47
4.	48.9	78.5	1.0523	0.3140	6.50
5.	48.9	78.6	1.0527	0.3135	7.25
6.	48.7	78.1	1.0498	0.3112	7.97
7.	48.6	77.7	1.0450	0.3055	8.98
		(Fig.4, Curve 8).			

TABLE No. 4.

Ferric chlorite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
(a). Readings with Sodium citrate.					
1.	54.3	138.0	1.3621	0.451	4.00
2.	51.2	88.3	1.1330	0.415	4.15
3.	50.8	85.8	1.1165	0.393	5.15
4.	50.5	80.1	1.0830	0.352	6.00
5.	50.2	75.3	1.0527	0.314	7.00
6.	50.0	72.6	1.0373	0.295	7.95
7.	49.7	71.3	1.0240	0.278	8.50
(Fig. 6 ,Curve 1).					
(b).Readings with Na_2SO_4					
1.	52.2	89.0	1.1560	0.443	4.02
2.	50.3	88.5	1.1213	0.400	4.73
3.	49.7	86.8	1.1062	0.381	5.14
4.	49.3	81.4	1.0710	0.337	6.02
5.	49.0	75.6	1.0397	0.299	7.00
6.	48.5	73.8	1.0220	0.276	8.00
7.	48.2	72.0	1.0099	0.261	8.47
(Fig.6, Curve 2).					
(c).Readings with Sodium acetate.					
1.	51.1	91.2	1.1472	0.432	4.00
2.	50.7	85.0	1.1095	0.385	4.75
3.	50.5	80.7	1.0871	0.357	5.25
4.	50.2	77.3	1.0647	0.329	6.05
5.	50.0	72.6	1.0352	0.292	7.00
6.	49.8	69.3	1.0125	0.263	8.00
7.	49.5	79.5	1.0040	0.253	8.51
(Fig.6,Curve 3).					
(d).Readings with NaCl.					
1.	51.4	106.9	1.2120	0.513	4.02
2.	51.0	89.7	1.1380	0.421	4.65
3.	49.9	85.5	1.1000	0.374	5.17
4.	49.7	78.6	1.0652	0.330	5.95
5.	49.5	72.4	1.0273	0.282	6.92
6.	49.3	69.1	1.0041	0.253	7.95
7.	49.1	67.0	0.9910	0.237	8.50
(Fig.6 ,Curve 4).					

VISCOSITY VARIATIONS WITH þH IN FERRIC-CHLORITE IN PRESENCE OF FIXED AMOUNT OF ANIONS

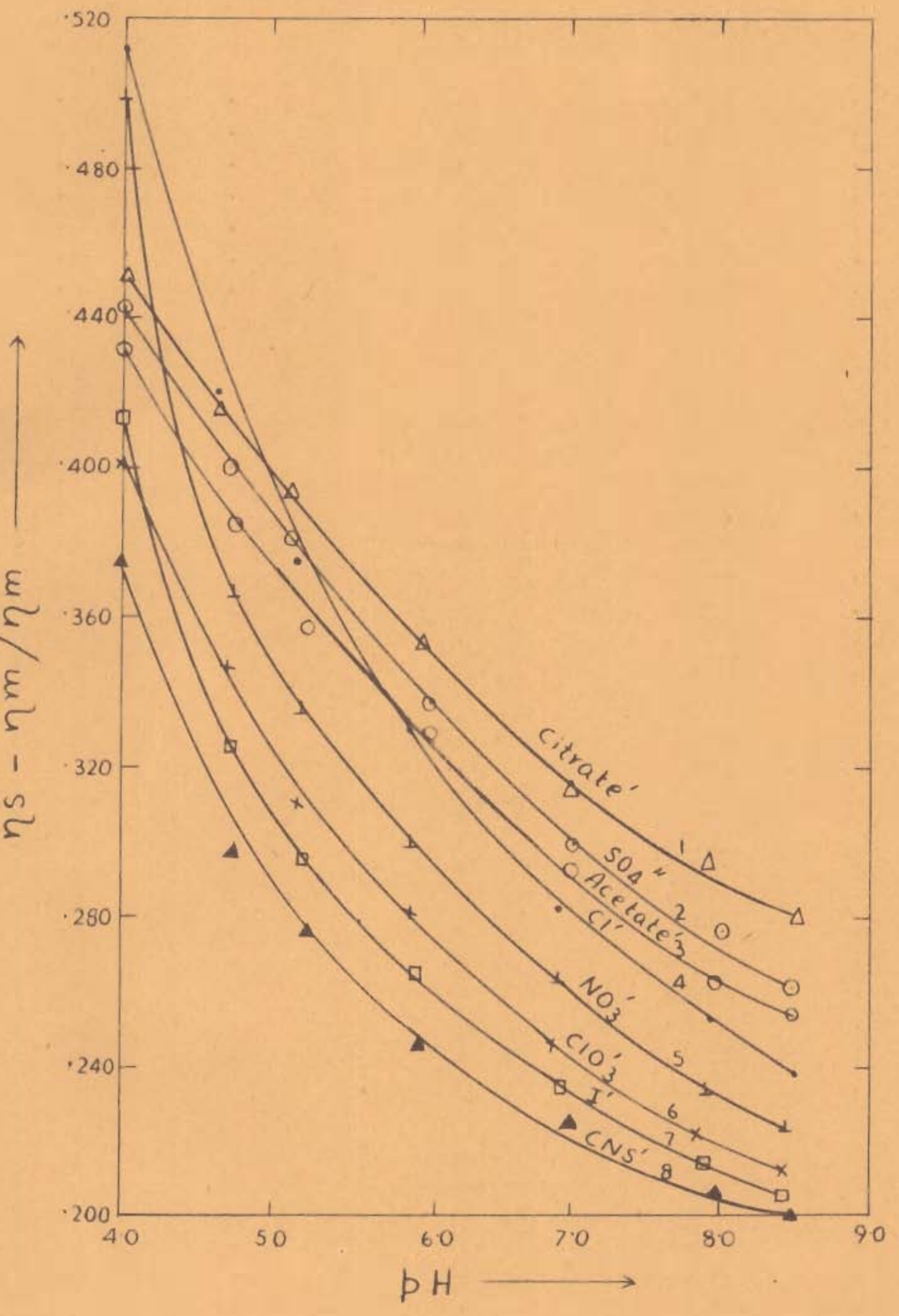


FIG. 6

TABLE No. 4.

Ferric chlorite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
		(e). Readings with $NaNO_3$.			
1.	53.5	81.1	1.2000	0.499	4.00
2.	50.5	82.3	1.0933	0.365	4.75
3.	50.3	77.7	1.0682	0.334	5.15
4.	50.0	73.2	1.0399	0.299	5.95
5.	49.7	69.3	1.0125	0.263	6.92
6.	49.4	66.1	0.9883	0.233	7.90
7.	49.2	65.5	0.9802	0.224	8.45
		(Fig.6, Curve 5).			
		(f). Readings with $NaClO_3$.			
1.	50.2	89.0	1.1220	0.401	4.00
2.	49.5	81.7	1.0783	0.346	4.70
3.	49.3	77.0	1.0492	0.310	5.20
4.	49.1	63.1	1.0263	0.281	5.95
5.	48.9	67.5	0.9912	0.247	6.92
6.	48.8	65.4	0.9795	0.222	7.90
7.	48.5	64.7	0.9699	0.211	8.45
		(Fig.6, Curve 6).			
		(g). Readings with NaI.			
1.	54.5	80.0	1.1323	0.413	4.01
2.	51.3	74.5	1.0615	0.325	4.75
3.	51.0	70.9	1.0381	0.296	5.25
4.	50.8	67.7	1.0134	0.265	6.00
5.	50.5	64.1	0.9882	0.234	6.92
6.	50.2	62.1	0.9711	0.212	7.90
7.	49.9	61.8	0.9655	0.205	8.45
		(Fig.6, Curve 7).			
		(h). Readings with NaCNS.			
1.	52.3	72.8	1.1007	0.375	4.02
2.	51.7	69.6	1.0383	0.297	4.75
3.	51.5	67.3	1.0226	0.276	5.25
4.	51.1	64.4	0.9973	0.245	6.00
5.	50.9	63.2	0.9826	0.226	7.00
6.	50.8	60.6	0.9673	0.208	7.95
7.	50.7	60.1	0.9620	0.201	8.50
		(Fig.6, Curve 8).			

TABLE No. 5.

Aluminum chlorite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
		(a). Readings with Sodium citrate.			
1.	41.4	70.6	0.9128	0.1400	4.02
2.	41.3	70.4	0.9108	0.1375	4.80
3.	41.1	70.6	0.9089	0.1351	5.50
4.	41.1	70.8	0.9096	0.1360	6.25
5.	41.3	70.6	0.9117	0.1386	7.05
6.	41.5	70.7	0.9143	0.1416	8.07
7.	41.7	70.9	0.9188	0.1475	9.00
		(Fig.7, Curve 1).			
		(b). Readings with Na_2SO_4.			
1.	39.8	73.0	0.9007	0.1348	4.02
2.	39.9	74.6	0.9094	0.1357	4.74
3.	40.1	74.3	0.9115	0.1383	5.45
4.	40.1	74.6	0.9127	0.1397	6.25
5.	40.2	74.8	0.9147	0.1424	7.10
6.	40.3	75.1	0.9178	0.1462	8.07
7.	40.4	75.5	0.9207	0.1498	8.95
		(Fig.7, Curve 2).			
		(c). Readings with Sodium acetate.			
1.	41.2	69.6	0.9054	0.1308	4.11
2.	41.6	68.9	0.9152	0.1430	4.85
3.	41.7	71.0	0.9190	0.1477	5.07
4.	41.8	71.2	0.9210	0.1502	6.50
5.	41.7	70.9	0.9185	0.1471	7.13
6.	41.6	68.9	0.9152	0.1430	8.15
7.	41.3	70.2	0.9098	0.1362	9.00
		(Fig.7, Curve 3).			
		(d). Readings with NaCl.			
1.	39.7	71.0	0.8907	0.1123	4.00
2.	41.2	71.2	0.9128	0.1400	4.73
3.	41.3	71.7	0.9168	0.1450	5.48
4.	41.3	71.7	0.9168	0.1450	6.25
5.	41.2	71.6	0.9147	0.1424	6.97
6.	41.1	71.4	0.9120	0.1390	7.95
7.	39.9	74.1	0.9072	0.1325	8.75
		(Fig.7, Curve 4).			

VISCOSITY VARIATIONS WITH pH IN ALUMINIUM CHLORITE IN PRESENCE OF FIXED AMOUNT OF ANIONS

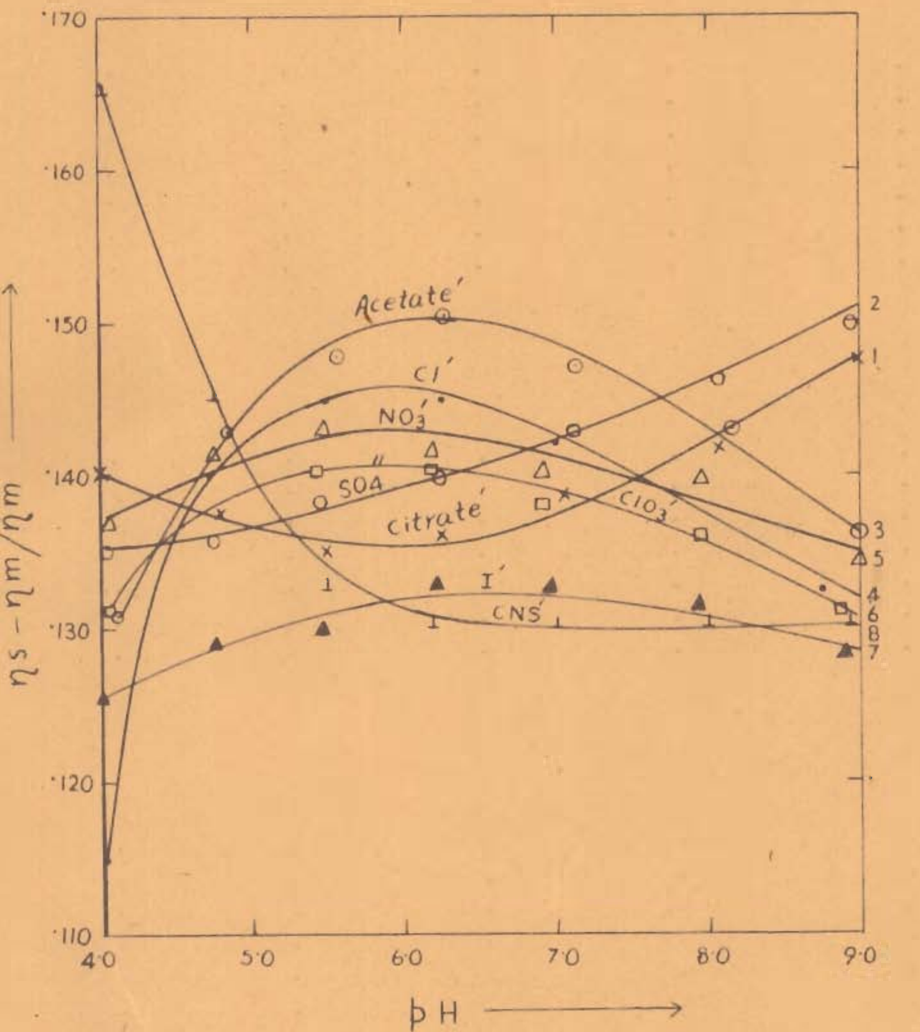


FIG. 7

TABLE No. 5.

Aluminum chlorite clay sol.

Sl.No.	Time of rise. seconds.	Time of fall. seconds.	η_s centi-poise.	$\eta_s - \eta_m / \eta_m$	pH
(e). Readings with $NaNO_3$.					
1.	41.3	70.3	0.9104	0.1370	4.05
2.	41.5	70.6	0.9138	0.1412	4.75
3.	41.6	70.4	0.9144	0.1430	5.48
4.	41.5	70.6	0.9140	0.1415	6.20
5.	41.4	70.6	0.9128	0.1400	6.90
6.	41.4	70.5	0.9127	0.1398	7.95
7.	41.0	70.3	0.9059	0.1345	9.00
(Fig.7, Curve 5).					
(f). Readings with $NaClO_3$.					
1.	41.0	70.4	0.9061	0.1316	4.05
2.	41.4	70.3	0.9116	0.1385	4.77
3.	41.5	70.4	0.9132	0.1405	5.42
4.	41.5	70.4	0.9132	0.1405	6.15
5.	41.3	70.3	0.9102	0.1380	6.90
6.	41.2	70.5	0.9096	0.1360	7.95
7.	41.0	70.3	0.9057	0.1312	8.85
(Fig.7, Curve 6).					
(g). Readings with NaI.					
1.	40.6	70.5	0.9011	0.1254	4.02
2.	40.8	70.4	0.9040	0.1290	4.51
3.	40.8	70.5	0.9048	0.1300	5.47
4.	40.9	70.8	0.9070	0.1327	6.20
5.	40.9	70.8	0.9070	0.1327	6.97
6.	40.8	71.0	0.9060	0.1315	7.92
7.	40.7	70.4	0.9032	0.1280	8.90
(Fig. 7, Curve 7).					
(h). Readings with NaCNS.					
1.	43.2	69.7	0.9328	0.1650	4.02
2.	41.3	71.7	0.9168	0.1450	4.77
3.	39.9	74.1	0.9074	0.1325	5.50
4.	39.7	74.2	0.9048	0.1300	6.15
5.	39.7	74.2	0.9048	0.1300	7.00
6.	39.7	74.2	0.9048	0.1300	8.00
7.	39.7	74.2	0.9048	0.1300	8.92
(Fig. 7, Curve 8).					

RESULTS

1. Bentonite:- (Fig. 1 a and b.).

The effect of the cations, calcium, potassium and sodium, on the viscosity is a continuous increase following the order calcium > potassium > sodium; calcium giving the highest viscosity.

With all the anions, there is a sharp initial decrease in viscosity between the pH range of 2.8-4.8; order of the anions is $SO_4 > NO_3 > ClO_3 >$ citrate > CNS > Cl > I at a pH of 7.0; sulphate giving the highest viscosity. After pH 4.8 the viscosity remains almost constant upto a pH of 10.8.

2. Magnesium chlorite:- (Figs. 2 a and 3).

As in case of bentonite, here also, the effect of the cations, on viscosity, is a continuous increase with the same order of cations.

Almost similar curves are obtained with all anions, showing an initial decrease, reaching a minimum value between pH 6-7, after which the viscosity continuously increases. The highest viscosity is observed with citrate ions, the order being: citrate $> SO_4 >$ Acetate $> Cl > NO_3 > ClO_3 >$ I > CNS.

3. Ferric chlorite:- (Figs.5 a and 6).

As in the first two cases, the effect of the cations investigated is the same.

Like, magnesium chlorite, here also, similar curves are obtained for all the anions employed. Order of the anions is also the same as in case 2. The viscosity, in this case, continuously falls off, without showing any increase over the entire pH range investigated.

4. Nickel chlorite:- (Figs. 2 b and 4).

Its behaviour is, also, similar to that of magnesium chlorite, as regards the effect of cations and the order of anions. However, unlike magnesium chlorite, here the viscosity first increases upto pH 6.5 and then continuously falls between the pH range 7.0 - 9.0. A maxima in viscosity is observed in all the cases between pH 6-7.

5. Aluminum chlorite:- (Figs. 5 b and 7).

Like all the other clays investigated, here also the effect of cations, is a continuous increase in viscosity, with the same order of the cations.

The shape of the pH-viscosity curves is dependant on the nature of the anion employed. With anions, acetate $>$ $Cl > NO_3 > ClO_3 > I$, the viscosity first increases and then decreases, exhibiting a maxima, the position of which changes with the nature of the anion. With CNS the viscosity first decreases and then remains almost constant between pH 6-9. With citrate the viscosity first shows a decrease and then a continuous increase. With SO_4 ion the viscosity increases continuously.

DISCUSSION

The concept of two types of electrical double layers in clay suspensions, the negative layer arising out of faces and the positive one from the edges, is now a fairly accepted one. Although, initially it was enunciated for explaining the behaviour of kaolinite (263), the concept of a positive double layer has been introduced for montmorillonite suspensions in view of two crystallographically different surfaces.

Chlorites, which are modified montmorillonite clay structures, can also be treated from the view point of two electrical double layers concept. The mica units can be considered to carry a negative charge, due to the substitution of Al for Si ; whereas the brucite layer or any other bivalent metal hydroxide layer would carry a positive charge. This picture would, however, differ when substitutions with trivalent ions like Fe^{+3} ions take place of the whole brucite layer. Under these conditions the negative electrical double layer would be more dominant and face to face association would play a major role. Otherwise, both face to face and edge to edge or edge to face associations will be operative and control the flow properties of the clay suspensions.

Unlike ordinary colloidal solutions, where the effect of the addition of electrolytes, acids or alkalies, is discussed only in terms of sensitization, coagulation and peptization, a few more factors, which in certain cases, may be very effective, should also be considered. These are (i) existence of agglomerates in the salt free sol in the form of T shaped duplets or triplets, conferring high viscosity to the system, (ii) formation of conglomerates by EE and FF association resulting in an increase in viscosity of even very dilute clay suspensions, (iii) FF association resulting in the formation of aggregates which lower the viscosity of the clay suspension.

All these factors, besides, the variation in the charge and zeta potential of the electrical double layers have to be considered in situ, when discussing the results of the variations in viscosity by the addition of electrolytes.

Viscosity variations on the gradual addition of alkalies to different clay suspensions, originally adjusted to pH 7.0: -(Figs. 1 a, 2 a and b, 5 a and b).

From the plots, of viscosity versus concentration, it is evident that the viscosity continuously increases with increase in concentration of the alkali. This indicates absence of peptizing effect by the OH^- ions of the alkali on the negative layer and charge reversal on the positive layer of the clay particles. This increase may be explained in terms of the simultaneous decrease in charge of the two layers by Na^+ and OH^- ions accompanied by association in which EE or EF association is more dominant. A peculiar behaviour of these alkali additions is that no initial decrease in viscosity is observed which is characteristic of all clay systems containing small amounts of electrolytes. The OH^- ions are known to exert a less pronounced peptizing effect than the anions of other electrolytes. To verify this, as well as to investigate the effect of the anions of the Hofmeister series, viscosity variations at different pH values in presence of a fixed amount of electrolytes were studied.

With all the three alkalies, $Ca(OH)_2$, KOH and NaOH, a continuous increase is observed in viscosity, in all the clay structures studied. The highest viscosity is achieved with $Ca(OH)_2$,whereas NaOH gives the least viscosity of the three. These results are in conformity with those of Gedroiz (264) and Tuorila (265).

Viscosity variations at different pH values in presence of a fixed amount of anion of the Hofmeister series:

1. Bentonite: (Fig.1 b).

The initial decrease in viscosity is due to the small amount of electrolyte already present. Its presence brings about a decrease in the charges of both the positive and negative layers,at the same time resulting in a decrease in the EF association forces and a large increase in the EF repulsive forces. In the higher pH range the OH^- ions do not exert the same flocculating effect when added as such. Anions of the Hofmeister series peptize the sol, thereby keeping the viscosity constant after the initial decrease.

2. Magnesium chlorite:(Fig. 3).

An initial decrease in viscosity (reaching a minimum value between pH 6-7 followed by a continuous increase is observed. This decrease in viscosity can be explained in a manner similar to that of bentonite. However, the increase is due to the fact that the brucite layer, in this case, has got a net positive charge and can easily attract OH^- ions on its surface. This could result in EE association and subsequent increase in viscosity.

3. Ferric chlorite: (Fig. 6).

Here also the order of anions bringing variations in viscosity is the same but no increase in viscosity in the higher pH range is observed. Instead, there is a continuous decrease. As already stated, substitution of Fe^{+3} ions for Al^{+3} ions would not bring about any change in the metal hydroxide layer, electrostatic forces would not be operative and simple adsorption of the anions of the Hofmeister series would take place.

4. Nickel chlorite : (Fig. 4).

Its behaviour is also similar to that of magnesium chlorite as regards the order of anions, but for the difference (from magnesium chlorite) that here the viscosity first increases and then continuously decreases. This difference, inspite of the fact that substitution by divalent cations takes place in both the cases,(the brucite layer has either $Mg(OH)_2$ or $Ni(OH)_2$), is due to the fact that $Mg(OH)_2$ being highly soluble enters into the interlayers much more easily than $Ni(OH)_2$,which is fairly insoluble. The chlorite structure thus obtained in this case will not be governed so much by the charge on the hydrous oxide layer than on the mica type layer. A behaviour intermediate between ferric chlorite and magnesium chlorite should, therefore, be observed in the flow properties of this transformed bentonite structure.

5. Aluminum chlorite : (Fig. 7).

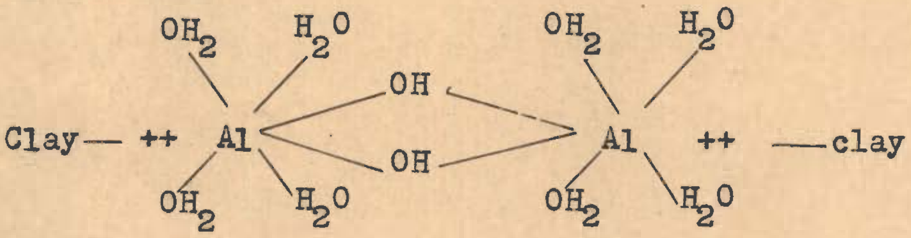
Here the behaviour is quite different from ferric chlorite inspite of the fact that trivalent cations are involved in the brucite type layers of both the cases. Here not only the order of anions is changed but an initial increase instead of decrease is observed. This may be due to the unique position of aluminum in clay structures. This atom is of such a size that it accomodates itself both to tetrahedral and octahedral coordination with oxygen; besides being extremely insoluble is amphoteric in character. In the acid range the layer will be positively charged with the result that with progressive addition of the alkali (i.e., increase in pH) its flocculation would take place resulting in increase in viscosity. At higher pH the hydroxide layer of the chlorite becomes negatively charged due to peptization by OH^- ions.

With CNS and citrate ions the peptization effect is not so marked because either a constancy in viscosity or decrease followed by an increase is observed.

The influence of aluminum on the viscosity of the clay suspensions may also be understood by considering the reaction of Al^{+3} ions with sodium hydroxide. According to Russell (266) the exchangeable aluminum on clays is in sixfold coordination with water molecules. The addition of sodium hydroxide results in replacement of part of the water by hydroxyl ions. This unit appears to be unstable and combines with another similar unit by sharing two hydroxyl ions and losing two water molecules. The overall reaction would be

$$2\ Al\ (H_2O)_6^{+3} + 2\ (OH)^- \quad = \quad (Al_2\ (OH)_2\ (H_2O)_6\ )^{+4} + 6\ H_2O\ .$$

This process continues as more hydroxyl ions are added forming large polyvalent aluminum-hydroxyl-water complex ions. Sodium ions would be adsorbed on the clay as Al^{+3} becomes neutralized. A mechanism thus would be provided whereby clay particles could be bound together through a bond of the type



This bond accounts for the maximum, observed in the viscosity pH curves, as the amount of NaOH is increased. As sodium hydroxide is added in excess of that needed for complete neutralization of Al^{+3} ions, aluminum hydroxide would form thereby eliminating the bonding force between the clay particles and causing the viscosity to decrease.

Another explanation has been offered by Cashen (267) for these changes, taking into consideration the formation of single complexes as $(Al_6\ (OH)_{15}\ )^{+3}$ or $(Al_8\ (OH)_{20}\ )^{+4}$, whereby the clay particles will become positively charged near the periphery by an excess of the complex ions in the Stern Layer, resulting in an increased edge to face attraction and hence viscosity.

It is apparent from a consideration of the viscosity behaviour of these natural and modified clay structures that gels are formed under suitable conditions. The type of structure formed is, probably, the brush heap in which the gel is made up of interlaced particles throughout the system and with the dispersion medium being held in the mass by capillary forces. This structure implies that the clay particles are of a hetrophilic nature i.e., the particles contain areas both of a hydrophilic character and also of a hydrophobic character. If the particles were hydrophilic over the entire surface there would be no possibility of particle to particle contact. In the opposing situation, in which the surface is entirely hydrophobic, complete contact could take place and dense floccules would form. According to this mechanism it is obvious that the interaction of clay particles may be altered by any condition that would change the ionization of the hydrophobic part or would change the ratio of the hydrophobic to hydrophilic part.

Studying the viscosity-pH curves of these transformed clays it is seen that the order of the Hofmeister series of anions is rigorously followed in all the four transformed clays. The order in case of magnesium, ferric and nickel chlorite is citrate $> SO_4 >$ acetate $> Cl > NO_3 > ClO_3 > I > CNS$, and for aluminum chlorite it is acetate $> Cl > NO_3 > ClO_3 > I$; CNS, citrate and SO_4 showing an abnormal behaviour, whereas in case of bentonite the Hofmeister series is not followed.

Also comparing the shapes of the various viscosity -pH curves of these clays amongst themselves and also with bentonite one can distinguish between these.

From all these observations it can definitely be decided that the original bentonite structure has been changed to a different structure and these transformed structures are also different in their rheological behaviour towards different electrolytes. It is interesting to find that no differentiation of these clays amongst themselves or from bentonite can be affected on the basis of their viscosity data with $Ca(OH)_2$, KOH and NaOH, as the behaviour of all these is very similar.

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CHAPTER IV

Wiegner Pallmann Suspension Effect in transformed montmorillonite structures (chlorites).

INTRODUCTION

Origin of suspension effect:

It is a well known fact that the e.m.f. reading, obtained on a suspension, with a glass-calomel electrode assembly, usually, differs from that obtained on the equilibrium solution of the suspension. Also, coarse suspensions, particularly those of clayey materials, are known to show marked differences in hydrogen ion concentrations, at different depths of the suspensions. This phenomenon, first observed by Wiegner (128) and later on worked out by Pallmann (132), as to include other lyophobic colloidal systems, has been named as the "suspension effect". De Bruyn (130) has, however, termed it as the "sol concentration effect". The same phenomenon has also been observed when the suspension is centrifuged, (139) or coagulated by a neutral salt, (129).

Suspension effect has been shown to depend on the nature of the dispersed phase the concentration of the electrolyte used for coagulation, the pH of the suspension and the method of measuring the pH, (139 a). Although Unmack (133) has refused to accept the existence of this effect, but the well established data of Wiegner and Pallmann (128,129,132), Gatovskaya and Vasilev (134), Nikolskii (135), Sollner (136), Overbeek (137), Bloksma (138), Voiteskhovskii and Vovnenko (139), as also the unpublished work of Loosjes (131), and Van Laar (268) support, not only the qualitative existence of this effect, but also give several empirical relationships between the pH and the concentration of the suspension, Theory of membrane equilibrium has mostly been used to interpret the data.

Positive and negative suspension effect:

The variation in pH, with soil water ratio, was carefully investigated by potentiometric and inversimetric methods, by Wiegner and Pallmann, who found that in acidic systems, the pH of the suspension was lower than that of the ultrafiltrate or the clear supernatant liquid(designated in this thesis as positive suspension effect). At low concentration of acidic colloid the hydrogen ion activity calculated from the pH was found to be a linear function of concentration, but it was true only over a limited range. Wiegner and Pallmann, also, investigated the relationship of pH and concentration for alkaline systems, in which case Christenson and Jensen (269) had found the filterate to be more acidic than the soil water system (designated here as negative suspension effect). Wiegner and Pallmann have compared the three methods for these investigations, (a) potentiometric determinations, (b) cataphoretic determination of the zeta potential, (c) quantitative exchange experiments against salt solutions of varying concentration. The reaction of the disperse phase (acidic or alkaline) does not, always, determine the kind of suspension effect(positive or negative). The zeta potential is independent of the suspension effect. All negatively charged systems liberate more hydrogen than hydroxyl, whereas the reverse is true of the positively charged systems.

Explanation for suspension effect:

Explaining their results, Wiegner and Pallmann, suggested that the difuse double layer could be regarded, as consisting of an outer and an inner strongly absorbed part. The outer part determines the sign of the zeta potential and the dominance of hydrogen or hydroxyl ion in exchange against a salt. As was demonstrated for charcoal, the same system can change over from the acid to the alkaline suspension effect, by the addition of a base, carrying a negative zeta potential throughout and also it was considered that the suspension effect and the Donnan Effect are identical, for systems at equilibrium(270,271). Tschapek (270) noted the reversing effect of quadrivalent thorium ions on the Donnan Membrane Potential. Peech et al. (141) have shown that a Na-clay showing the normal behaviour, changed over to the alkaline suspension effect when saturated with calcium and recorded the case of "reversed suspension effect", where one acidic clay gave a Donnan potential of opposite sign, from that expected by the normal suspension.

The evidence, so far available, on the alkaline suspension effect, strongly indicates, that free energy considerations really determine when it comes into play. If, when a small amount of hydroxide is added to an infinite amount of the clay, the free energy change, due to adsorption of hydroxyl, exceeds that due to incorporation of the metallic ion, then the alkaline effect will show itself.

Wiegner and Pallmann had ascribed this suspension effect to an adsorption of H^+ ions. Now the evidence, that this difference in e.m.f., manifests itself through the junction potential between the suspension and the KCl of the salt bridge employed with the calomel electrode is strongly prevailing,(140,141). A hypothesis of this kind has been put forward by Loosjes (131) and Overbeek (137). Overbeek's empirical relationship has been tested by Bower (142) and Bloksma (138).

Overbeek (137) had shown that the main contributing factor to this effect is the reduced mobility of the counter ions, owing to a retarding effect by the oppositely charged particle surfaces, but Pallmann's comparison (132) of potentiometric and inversimetric methods, for dilute clay systems, is against any modification of the mobility of these ions, The question,as to the site of the potential difference, observed in studies of the suspension effect was first raised by Jenny et al. (140), which set off a very lively controversy by different workers,(272-278).

<u>Theoratical calculation of suspension effect</u>:

Loosjes (131) has deduced the following equation for the suspension effect,

$(E_{cs} - E_{cs \to \infty})\ (cs + K) = (E_{cs = 0} - E_{cs \to \infty})\ K$ where E's are the e.m.f.'s measured between a calomel electrode, connected to the solution through a salt bridge and a reversible electrode, in the solution, cs is the sol concentration, in arbitrary units, and K is a constant.

Since the e.m.f.'s are linearly dependant upon the pH, an equivalent expression is

$$(pH_{cs} - pH_{cs \to \infty}) \; (cs + K) = (pH_{cs = 0} - pH_{cs \to \infty}) \; K.$$

Loosjes recalculated data from Pallmann (132), on hydrogen clay and the calculated pH values for different concentrations compare, very favourably, with the measured values.

Characterization of clay minerals from suspension effect:

Very recently Singhal and Malik (143) have used the suspension effect for the identification of clay minerals. From their measurements, in the acidic media, they concluded that the pH difference of the equilibrium liquid and the suspension for a particular clay concentration follows the order; montmorillonite > kaolinite > illite. This pH difference, when plotted against concentration, showed a uniform decrease in case of bentonite, while a gradual rise was observed with kaolin. No such regularity was observed in case of illite. Extending their work on various soils, they have shown that the Pallmann Effect can be usefully employed in showing the presence of different clay minerals in soil samples.

Suspension effect and the zero point of charge:

van Laar (268) has used this sol concentration effect in order to determine the zero point of charge of AgI. He determined the pAg, for which there was no difference in e.m.f. between a salt bridge in a AgI suspension and a salt bridge in the equilibrium solution. At this pAg, there was no diffuse double layer and when specific adsorption is absent, the zero point of charge is reached.

Mackor (279) while studying the influence of non electrolytes, on the shift of zero point of charge, has stressed on the shift, caused by acetone, resulting because of the change in potential, due to the oriented adsorption of acetone.

Aim of these investigations:

Assuming that factors like size and shape of the particles (139), presence of osmotically active contra-ions (192), and the relative adsorbability of hydrogen ions, in different layers of the clay suspensions, (132), are operative and that the peculiar phasal conditions of ions in suspensions, their transference numbers and their colloid chemical properties would considerably influence the pH measurements, it was thought worthwhile to apply this effect in determining the physical behaviour of these transformed clay structures as also to use it in their identification as suggested by Singhal and Malik (143). The investigations of this chapter, describe the results of suspension effect, as observed in acid and alkaline medium, both for natural and transformed clay systems. A few data for systems, studied in non-aqueous media, are also incorporated for the sake of comparison.

EXPERIMENTAL

Preparation of the clay sols:

The powdered clay samples were treated with 0.02 N HCl, in order to remove the free metal hydroxide and also to convert the clay in the hydrogen form. Utmost care was taken in this treatment, so that the structure of the transformed clays is not changed by the dissolution of alumina or silica. This was achieved by controlling the concentration of the acid used and the number of leachings. The clay was afterwards washed thoroughly with 75% alcohol water mixture and dried in the oven at 105°C. It was then taken up with either double distilled water or 90% ethyl alcohol and stirred in the mechanical shaker for two hours, after which the suspension thus obtained was centrifuged at 3000 r.p.m. for half an hour. The clear sol so obtained was passed through a generated column of Amberlite IR-120 in hydrogen form, to remove the last traces of any suspended metal hydroxide. All the necessary precautions were observed while using the ion exchange column regarding the regeneration, washing with the dispersion medium and also the time of contact etc..Concentration of the sol was determined in each case, as described earlier,and made constant to 0.75%.

Study of Pallmann Effect:

In the first set, different amounts(2 ml.to 14 ml.) of the clay sols(aqueous) were taken in about eight pyrex 50 ml. beakers, and the total volume was made up to 30 ml.

with double distilled water, no coagulant being added. After keeping the well stirred mixture of sol+water for two hours the pH of the whole suspension was measured, at 30 ± 0.01°C, with the help of a Cambridge Bench Type pH meter, along with Cambridge glass calomel electrode assembly.

In the second set, again, different amounts of the clay sols(2 ml. to 14 ml.) were taken in about eight (50 ml.) pyrex beakers. To each was added 5.0 ml.of saturated A.R. ammonium chloride solution in double distilled water or 90% ethyl alcohol, to act as a neutral coagulating salt. The volume was now made upto 30.0 ml. either by the addition of double distilled water or 90% ethyl alcohol. The beakers were well covered,after stirring with a clean glass rod, and kept undisturbed in a low temperature bath (approximately 5°C less than the room temperature), to avoid the loss of the dispersion medium, due to evaporation. After six hours the pH of the supernatant equilibrium liquid and the settled out coagulated suspension was measured (without disturbing the beakers) as above, at 30 ± 0.01°C. The pH of the equilibrium liquid was measured when the glass and calomel electrode assembly was just touching the top surface of the liquid, as this pH was found to vary with the depth of the solution. Similarly the pH of the suspension was measured when the electrodes were just touching the bottom of the beaker.

This procedure was followed throughout. Measurements in the acid range were made in this manner.

Measurements in the alkaline range were made under exactly similar conditions except that now in place of ammonium chloride, 5.0 ml. of 1 N NaOH in water or 90% ethyl alcohol were added.

All the experiments were performed in duplicate, to ensure accuracy of the results. Under exactly similar experimental conditions, blank experiments were also performed, using the dispersion medium in place of clay sols, which failed to show any similar effect.

The data obtained with the clay sols are given in the following tables:

TABLE No. 1.

Sol concentration effect.

pH of the hydrogen form of the clays in different dilutions in aqueous medium.

Conc. of the sol %	cs in arbitrary units.	Observed pH_{cs}	Calculated pH*	Observed pH_{cs}	Calculated pH	Observed pH_{cs}	Calculated pH
		Bentonite		Aluminum chlorite		Ferric chlorite	
0.0	00	6.69	6.69	6.71	6.71	6.69	6.69
0.05	10	4.87	4.72	5.48	5.58	5.15	5.11
0.10	20	3.98	3.90	4.92	4.84	4.65	4.71
0.20	40	3.00	3.09	3.90	4.00	4.07	4.00
0.25	50	2.94	2.88	3.75	3.68	3.75	3.76
0.30	60	2.75	2.70	3.50	3.45	3.51	3.42
0.40	80	2.50	2.49	2.99	3.10	3.30	3.36
0.50	100	2.35	2.26	2.83	2.80	3.25	3.20
0.75	150	2.20	2.20	2.51	2.51	3.00	3.00
			+K =16.13		K= 38.0		K = 23.3
			+$pH_{cs \longrightarrow \infty}$=1.65		$pH_{cs \longrightarrow \infty}$=1.40		$pH_{cs \longrightarrow \infty}$=2.42
			Fig.1, Curve 1.		Fig.1, Curve 2.		Fig.1, Curve 3.

\+ Mean values found from the various determined pH_{cs} values.

* Calculated using the equation

$$(pH_{cs} - pH_{cs \longrightarrow \infty})\ (cs + K) = (\ pH_{cs\ =\ 0} - pH_{cs \longrightarrow \infty})\ K.$$

Table contd..

TABLE No.1. (Contnued from Page 157).

Conc. of the sol %	cs in arbitrary units.	Observed pH_{cs}	Calculated pH	Observed pH_{cs}	Calculated pH
		Magnesium chlorite.		Nickel chlorite.	
0.0	00	6.72	6.72	6.70	6.70
0.05	10	5.40	5.31	4.90	4.80
0.10	20	4.61	4.71	4.43	4.37
0.20	40	4.08	4.16	3.99	4.08
0.25	50	3.92	4.00	3.94	4.00
0.30	60	3.85	3.90	3.96	3.96
0.40	80	3.69	3.76	3.90	3.91
0.50	100	3.57	3.66	3.83	3.86
0.75	150	3.50	3.50	3.80	3.80

Magnesium chlorite: $K = 15.2$

$pH_{cs \rightarrow \infty} = 3.20$

Fig.1, Curve 4.

Nickel chlorite: $K = 5.8$

$pH_{cs \rightarrow \infty} = 3.70$

Fig.1, Curve 5.

SOL CONCENTRATION EFFECT IN DIFFERENT CLAY MINERALS IN AQUEOUS MEDIUM

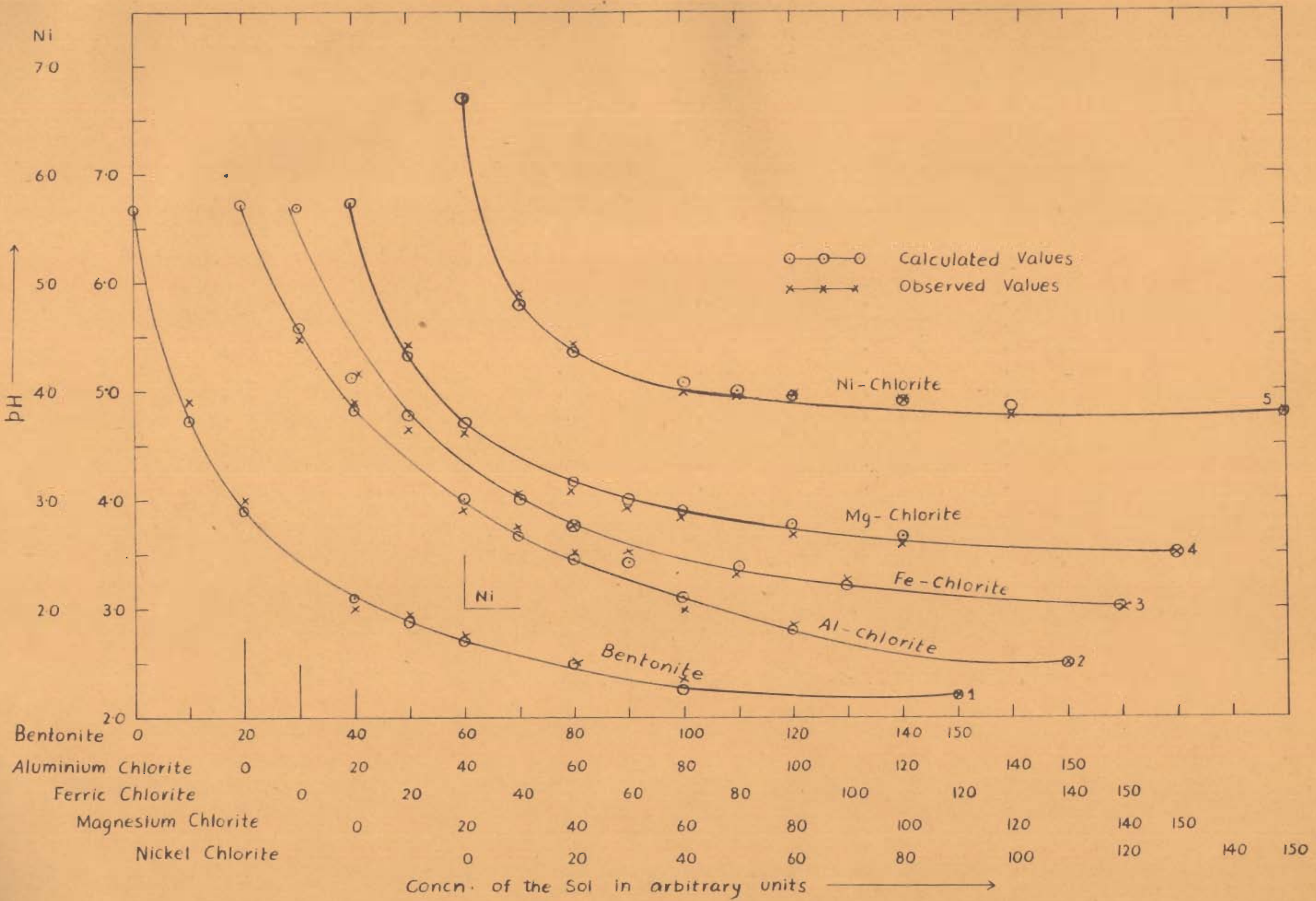


FIG. 1

TABLE No. 2.

Pallmann Effect in coagulated suspensions.

Hydrogen form of Bentonite.

Acidic range.

Amt. of the sol. ml.	Conc. %	pH of the equilibrium liquid. (upper layer).	pH of the suspension. (lower layer).	Difference in pH of the two layers. △ pH	pH of the equilibrium liquid. (upper layer).	pH of the suspension. (lower layer).	Difference in pH of the two layers. △ pH
		Aqueous medium.			Alcoholic medium.		
2.0	0.05	5.15	4.85	+ 0.30	5.00	4.85	+ 0.15
4.0	0.10	4.51	4.25	0.26	4.83	4.80	+ 0.03
6.0	0.15	3.98	3.75	0.23	4.69	4.75	- 0.06
8.0	0.20	3.59	3.40	0.19	4.62	4.75	- 0.13
10.0	0.25	3.27	3.12	0.15	4.56	4.75	- 0.19
12.0	0.30	2.99	2.87	0.12	4.45	4.70	- 0.25
14.0	0.35	2.68	2.60	0.08	4.35	4.65	- 0.30
		Fig.2 c, Curve 1.	Fig.2 b, Curve 1.	Fig.2 a, Curve 1.	Fig.3 c, Curve 1.	Fig.3 b, Curve 1.	Fig.3 a, Curve 1.

TABLE No. 3.

Pallmann Effect in coagulated suspensions.

Hydrogen form of Bentonite.

Alkaline range.

Amt. of the sol. ml.	Conc. %	pH of the equilibrium liquid. (upper layer).	pH of the suspension. (lower layer).	Difference in pH of the two layers. △ pH	pH of the equilibrium liquid. (upper layer).	pH of the suspension. (lower layer)	Difference in pH of the two layers. △ pH
		Aqueous medium.			Alcoholic medium.		
2.0	0.05	8.90	8.90	0.00	9.72	9.50	0.22
4.0	0.10	8.88	8.95	- 0.07	9.68	9.48	0.20
6.0	0.15	8.85	8.95	- 0.10	9.58	9.42	0.16
8.0	0.20	8.83	8.97	- 0.14	9.50	9.37	0.13
10.0	0.25	8.80	9.00	- 0.20	9.31	9.25	0.06
12.0	0.30	8.76	9.03	- 0.27	9.09	9.19	- 0.10
14.0	0.35	8.75	9.05	- 0.30	8.79	9.04	- 0.25
		Fig.4 c, Curve 1.	Fig.4 b, Curve 1.	Fig.4 a, Curve 1.	Fig.5 c, Curve 1.	Fig.5 b, Curve 1.	Fig.5 a, Curve 1.

TABLE No. 4

Pallmann Effect in coagulated suspensions.
Hydrogen form of aluminum chlorite.
(A) Acidic range.

Amt. of the sol. ml.	Conc. %	Upper layer. pH	Lower layer. pH	Difference △ pH	Upper layer. pH	Lower layer. pH	Difference △ pH
		Aqueous media.			Alcoholic media.		
2.0	0.05	5.60	5.50	0.10	5.42	5.90	- 0.48
4.0	0.10	5.12	4.90	0.22	5.58	5.87	- 0.29
6.0	0.15	4.76	4.45	0.31	5.69	5.86	- 0.17
8.0	0.20	4.47	4.07	0.40	5.77	5.86	- 0.09
10.0	0.25	4.20	3.73	0.47	5.81	5.86	- 0.05
12.0	0.30	3.98	3.45	0.53	5.84	5.86	- 0.02
14.0	0.35	3.77	3.20	0.57	5.84	5.85	- 0.01
		Fig.2 c, Curve 2,	Fig.2 b, Curve 2.	Fig.2 a, Curve 2.	Fig.3 c, Curve 2.	Fig.3 b, Curve 2.	Fig.3 a, Curve 2.

(B) Alkaline range.

Amt. of the sol. ml.	Conc. %	Upper layer. pH	Lower layer. pH	Difference △ pH	Upper layer. pH	Lower layer. pH	Difference △ pH
2.0	0.05	8.89	9.90	- 1.11	10.25	10.65	- 0.40
4.0	0.10	9.12	9.89	- 0.77	10.37	10.77	- 0.40
6.0	0.15	9.29	9.85	- 0.56	10.64	10.98	- 0.34
8.0	0.20	9.41	9.84	- 0.43	10.76	11.05	- 0.29
10.0	0.25	9.49	9.84	- 0.35	10.92	11.12	- 0.20
12.0	0.30	9.58	9.81	- 0.23	11.05	11.15	- 0.10
14.0	0.35	9.60	9.80	- 0.20	11.33	11.23	+ 0.10
		Fig.4 c, Curve 2.	Fig.4 b, Curve 2.	Fig.4 a, Curve 2.	Fig.5 c, Curve 2.	Fig.5 b, Curve 2.	Fig.5 a, Curve 2.

TABLE No. 5.

Pallmann Effect in coagulated suspensions.
Hydrogen form of ferric chlorite.
(A) Acidic range.

Amt. of the sol. ml.	Conc. %	Upper layer. pH	Lower layer. pH	Difference △ pH	Upper layer. pH	Lower layer. pH	Difference △ pH
		Aqueous media.			Alcoholic media.		
2.0	0.05	5.17	5.10	+ 0.07	6.44	6.82	- 0.38
4.0	0.10	4.93	4.75	0.18	6.62	6.82	- 0.20
6.0	0.15	4.72	4.45	0.27	6.69	6.81	- 0.12
8.0	0.20	4.50	4.15	0.35	6.74	6.81	- 0.07
10.0	0.25	4.32	3.90	0.42	6.78	6.81	- 0.03
12.0	0.30	4.13	3.65	0.48	6.80	6.81	0.00
14.0	0.35	3.94	3.40	0.54	6.82	6.80	+ 0.02
		Fig.2 c, Curve 3.	Fig.2 b, Curve 3.	Fig.2 a, Curve 3.	Fig.3 c, Curve 3.	Fig.3 b, Curve 3.	Fig.3 a, Curve 3.

(B) Alkaline range.

2.0	0.05	9.62	10.65	- 1.03	10.84	11.32	- 0.48
4.0	0.10	9.94	10.64	- 0.70	11.06	11.43	- 0.37
6.0	0.15	10.13	10.64	- 0.51	11.20	11.50	- 0.30
8.0	0.20	10.33	10.62	- 0.29	11.35	11.55	- 0.20
10.0	0.25	10.38	10.61	- 0.23	11.53	11.58	- 0.05
12.0	0.30	10.49	10.60	- 0.11	11.67	11.60	+ 0.07
14.0	0.35	10.52	10.60	- 0.08	11.78	11.61	+ 0.17
		Fig.4 c, Curve 3.	Fig.4 b, Curve 3.	Fig.4 a, Curve 3.	Fig.5 c, Curve 3.	Fig.5 b, Curve 3.	Fig.5 a, Curve 3.

TABLE No. 6.

Pallmann Effect in coagulated suspensions.
Hydrogen form of magnesium chlorite.

(A) Acidic range.

Amt. of the sol. ml.	Conc. %	Upper layer. pH	Lower layer. pH	Difference Δ pH	Upper layer. pH	Lower layer. pH	Difference Δ pH
		Aqueous media.			Alcoholic media.		
2.0	0.05	5.44	5.40	+ 0.04	6.45	6.95	- 0.50
4.0	0.10	5.09	4.95	0.14	6.53	6.95	- 0.42
6.0	0.15	4.83	4.60	0.23	6.65	6.95	- 0.30
8.0	0.20	4.60	4.30	0.30	6.70	6.95	- 0.25
10.0	0.25	4.47	4.11	0.40	6.80	6.95	- 0.15
12.0	0.30	4.30	3.93	0.45	6.87	6.95	- 0.08
14.0	0.35	4.14	3.70	0.54	6.90	6.95	- 0.05
		Fig.2 c, Curve 4.	Fig.2 b, Curve 4.	Fig.2 a, Curve 4.	Fig.3 c, Curve 4.	Fig.3 b, Curve 4.	Fig.3 a, Curve 4.

(B) Alkaline range.

Amt. of the sol. ml.	Conc. %	Upper layer. pH	Lower layer. pH	Difference Δ pH	Upper layer. pH	Lower layer. pH	Difference Δ pH
2.0	0.05	10.16	10.95	-0.79	10.90	11.50	- 0.60
4.0	0.10	10.39	10.94	-0.55	10.98	11.57	- 0.59
6.0	0.15	10.53	10.92	-0.39	11.05	11.60	- 0.55
8.0	0.20	10.71	10.92	-0.21	11.13	11.62	- 0.49
10.0	0.25	10.78	10.90	-0.12	11.28	11.65	- 0.37
12.0	0.30	10.80	10.86	-0.06	11.48	11.65	- 0.17
14.0	0.35	10.82	10.85	-0.03	11.72	11.67	+ 0.05
		Fig.4 c, Curve 4.	Fig.4 b, Curve 4.	Fig.4 a, Curve 4.	Fig.5 c, Curve 4.	Fig.5 b, Curve 4.	Fig.5 a, Curve 4.

TABLE No. 7.

Pallmann Effect in coagulated suspensions.
Hydrogen form of nickel chlorite.
(A) Acidic range.

Amt. of the sol. ml.	Conc. %	Upper layer. pH	Lower layer. pH	Difference Δ pH	Upper layer. pH	Lower layer. pH	Difference Δ pH
		Aqueous media.			Alcoholic media.		
2.0	0.05	5.32	5.30	+ 0.02	6.20	6.62	-0.42
4.0	0.10	5.13	5.03	0.10	6.35	6.60	-0.25
6.0	0.15	4.95	4.75	0.20	6.40	6.55	-0.15
8.0	0.20	4.75	4.50	0.25	6.43	6.52	-0.09
10.0	0.25	4.63	4.28	0.35	6.44	6.51	-0.07
12.0	0.30	4.50	4.11	0.39	6.45	6.50	-0.05
14.0	0.35	4.33	3.90	0.43	6.45	6.50	-0.05
		Fig.2 c, Curve 5.	Fig.2 b, Curve 5.	Fig.2 a, Curve 5.	Fig.3 c, Curve 5.	Fig.3 b, Curve 5.	Fig. 3 a, Curve 5.

(B) Alkaline range.

Amt. of the sol. ml.	Conc. %	Upper layer. pH	Lower layer. pH	Difference Δ pH	Upper layer. pH	Lower layer. pH	Difference Δ pH
2.0	0.05	9.52	10.50	-0.98	10.52	11.06	-0.54
4.0	0.10	9.89	10.49	-0.60	10.62	11.11	-0.49
6.0	0.15	10.17	10.47	-0.30	10.72	11.19	-0.47
8.0	0.20	10.35	10.46	-0.11	10.91	11.25	-0.34
10.0	0.25	10.36	10.42	-0.06	11.09	11.26	-0.17
12.0	0.30	10.38	10.41	-0.03	11.29	11.27	+0.02
14.0	0.35	10.40	10.40	-0.00	11.53	11.30	+0.23
		Fig.4 c, Curve 5.	Fig.4 b, Curve 5.	Fig.4 a, Curve 5.	Fig.5 c, Curve 5.	Fig.5 b, Curve 5.	Fig.5 a, Curve 5.

SUSPENSION EFFECT IN AOUEOUS MEDIUM, ACID RANGE, IN DIFFERENT CLAY MINERALS

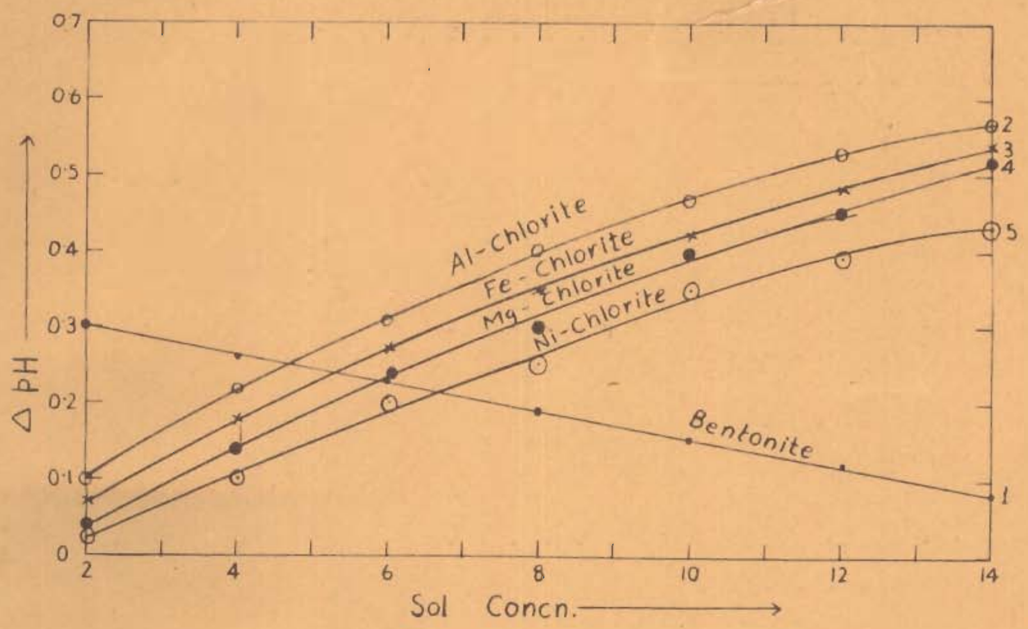


FIG · 2 (a)

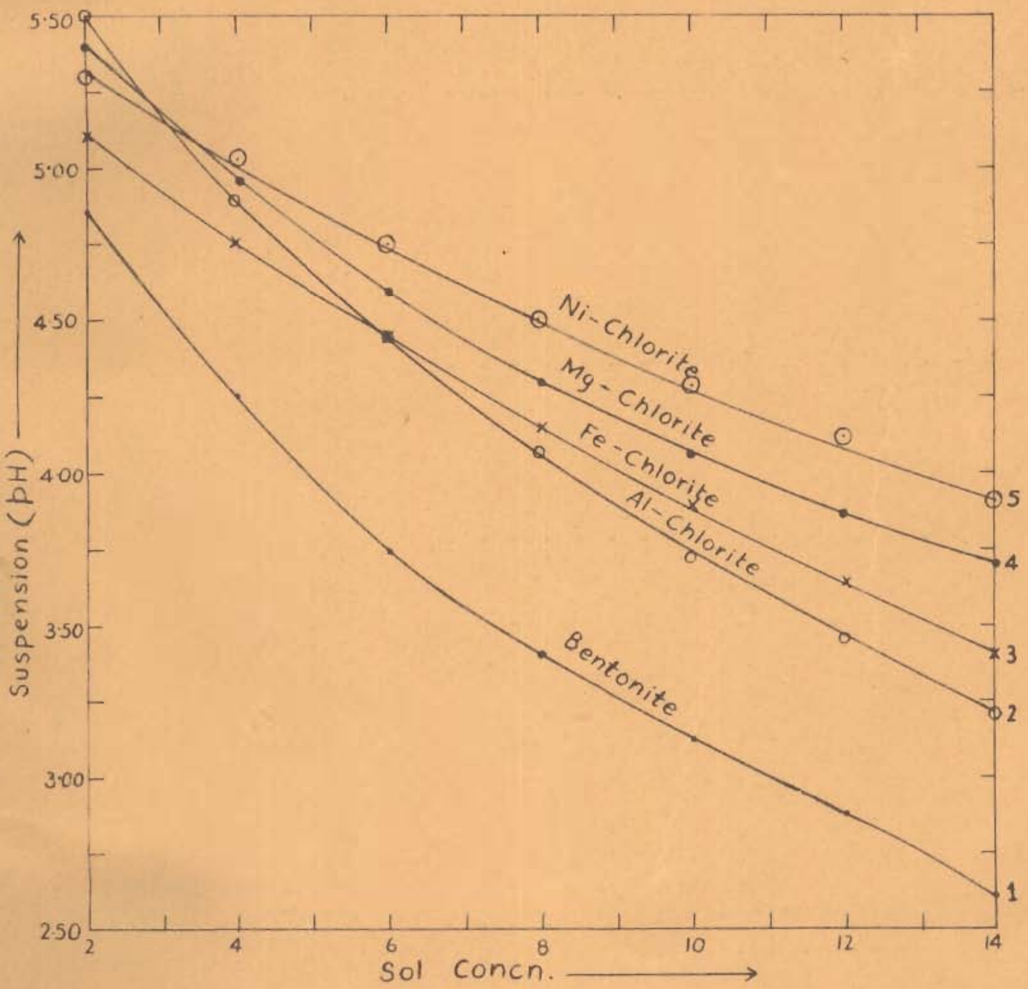


FIG · 2 (b)

SUSPENSION EFFECT IN AQUEOUS MEDIUM, ACID RANGE, IN DIFFERENT CLAY MINERALS .

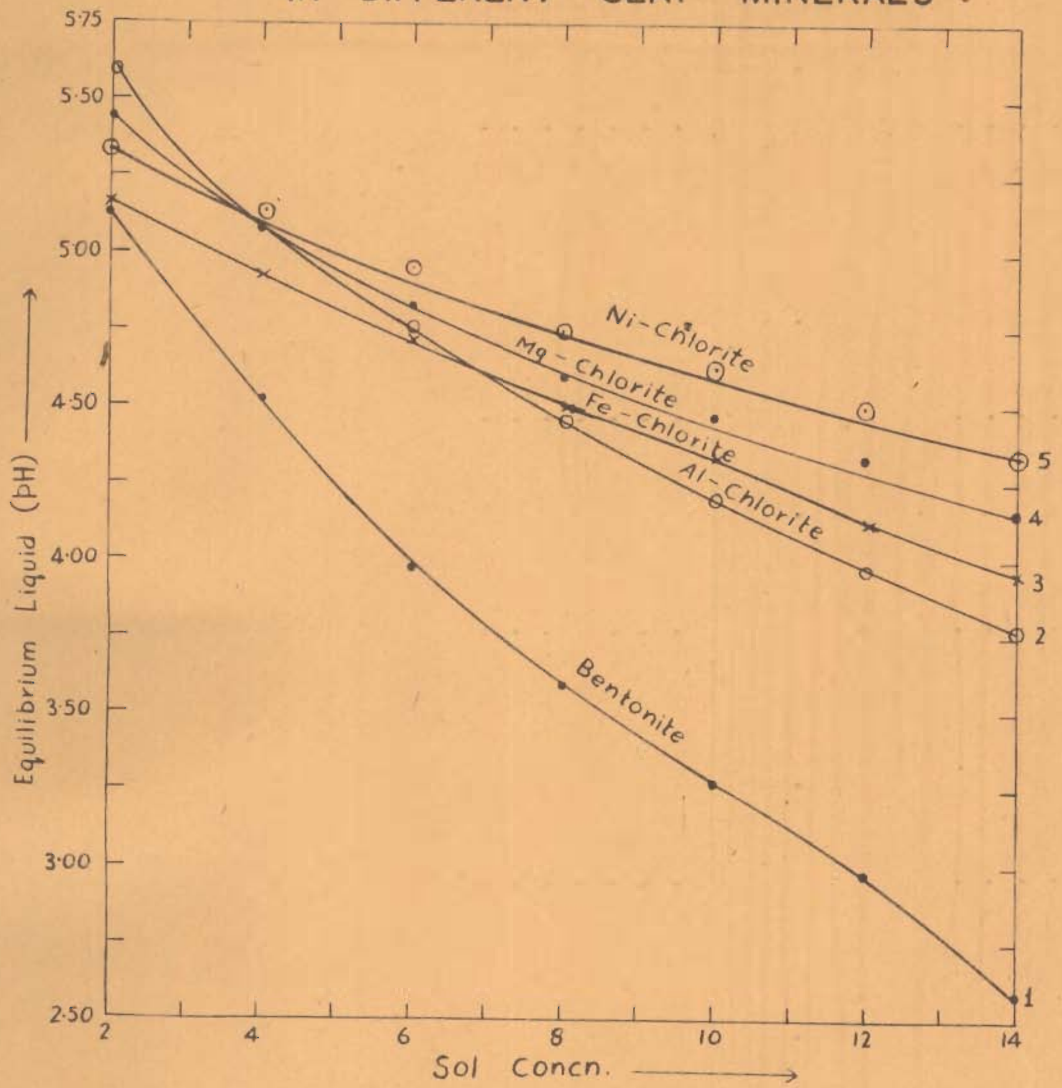


FIG. 2 (c)

SUSPENSION EFFECT IN ALCOHOLIC MEDIUM, ACID RANGE, IN DIFFERENT CLAY MINERALS

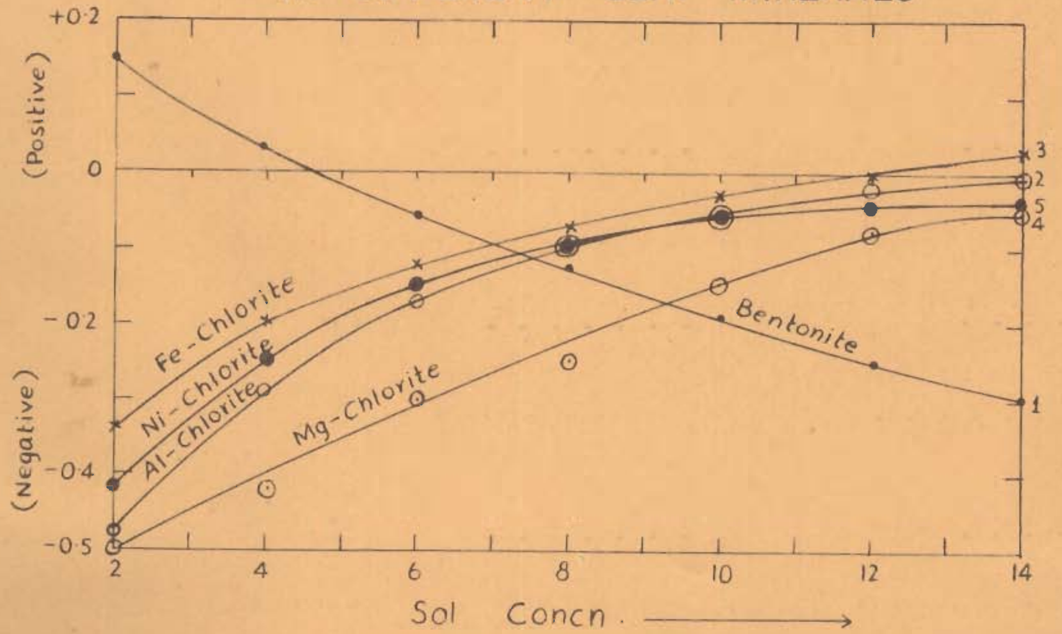


FIG 3(a)

SUSPENSION EFFECT IN ALCOHOLIC MEDIUM, ACID RANGE, IN DIFFERENT CLAY MINERALS

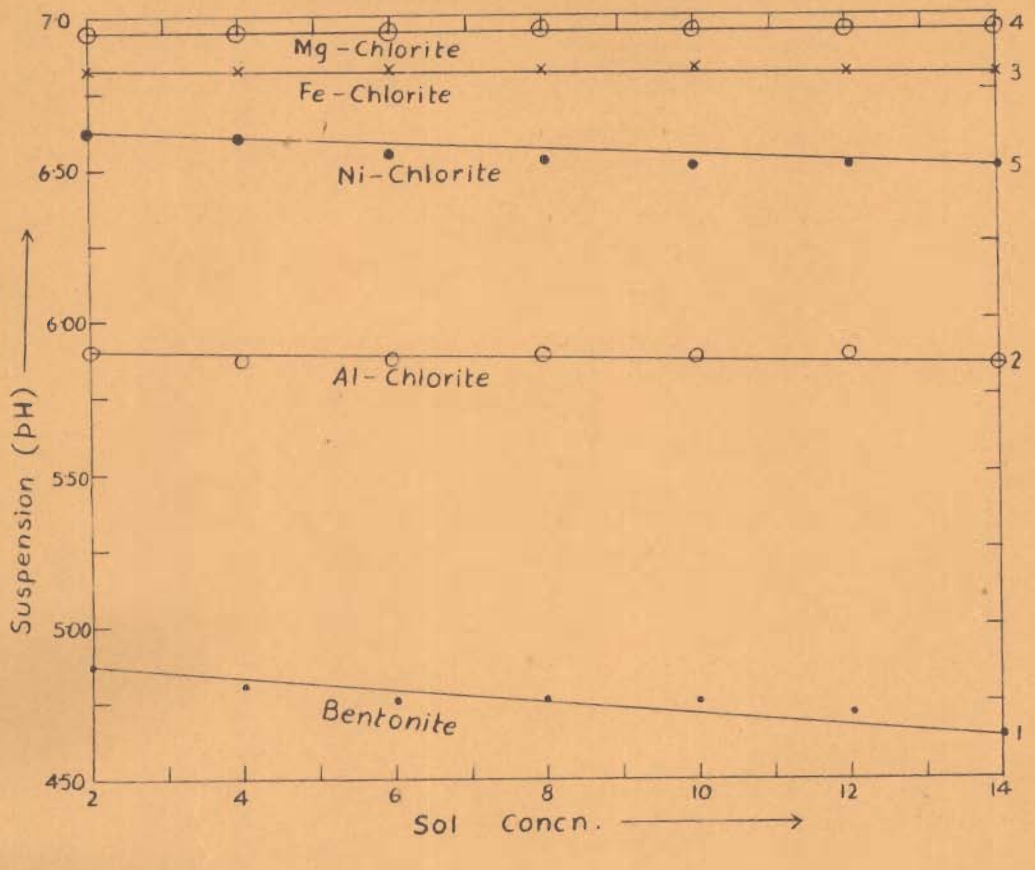


FIG · 3 (b)

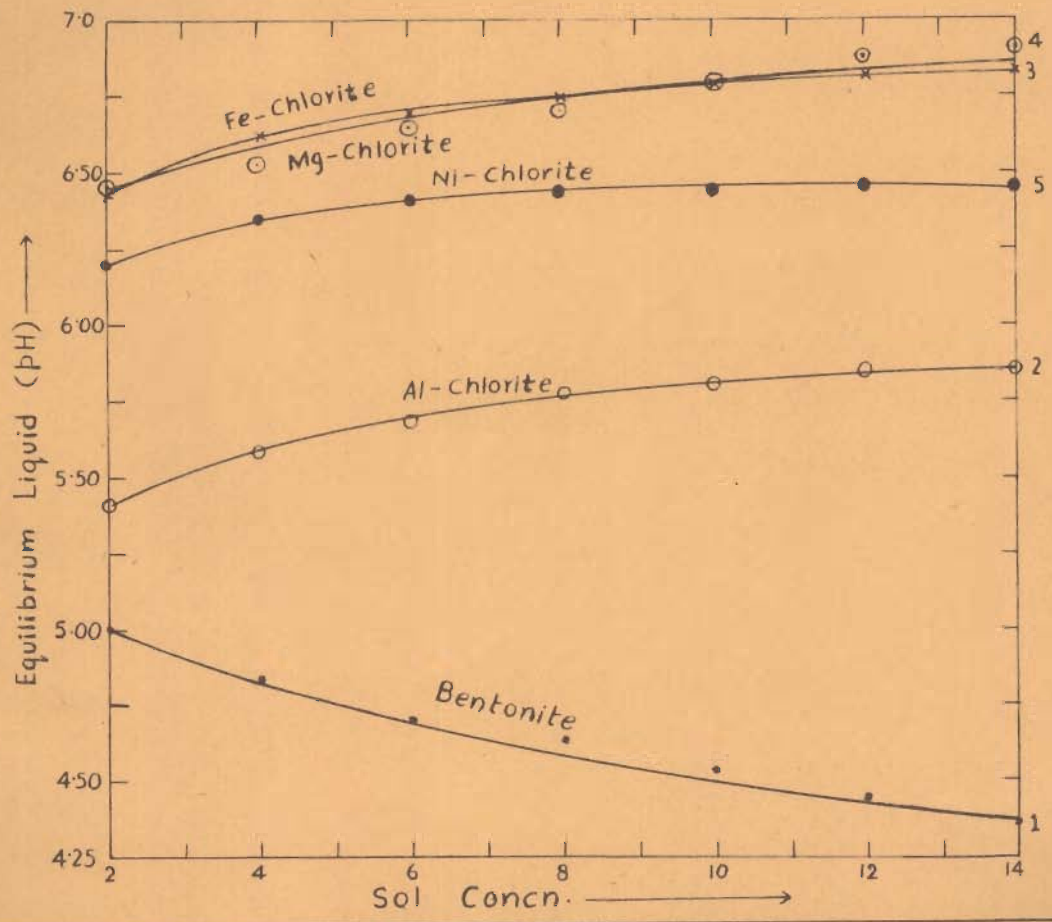


FIG · 3 (c)

SUSPENSION EFFECT IN AQUEOUS MEDIUM, ALKALINE RANGE, IN DIFFERENT CLAY MINERALS

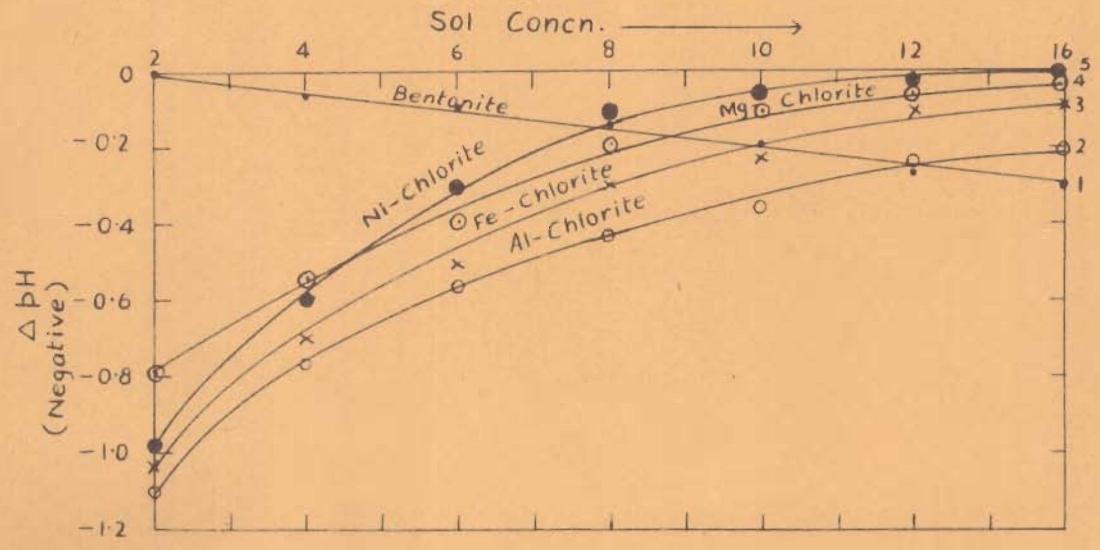


FIG. 4 (a)

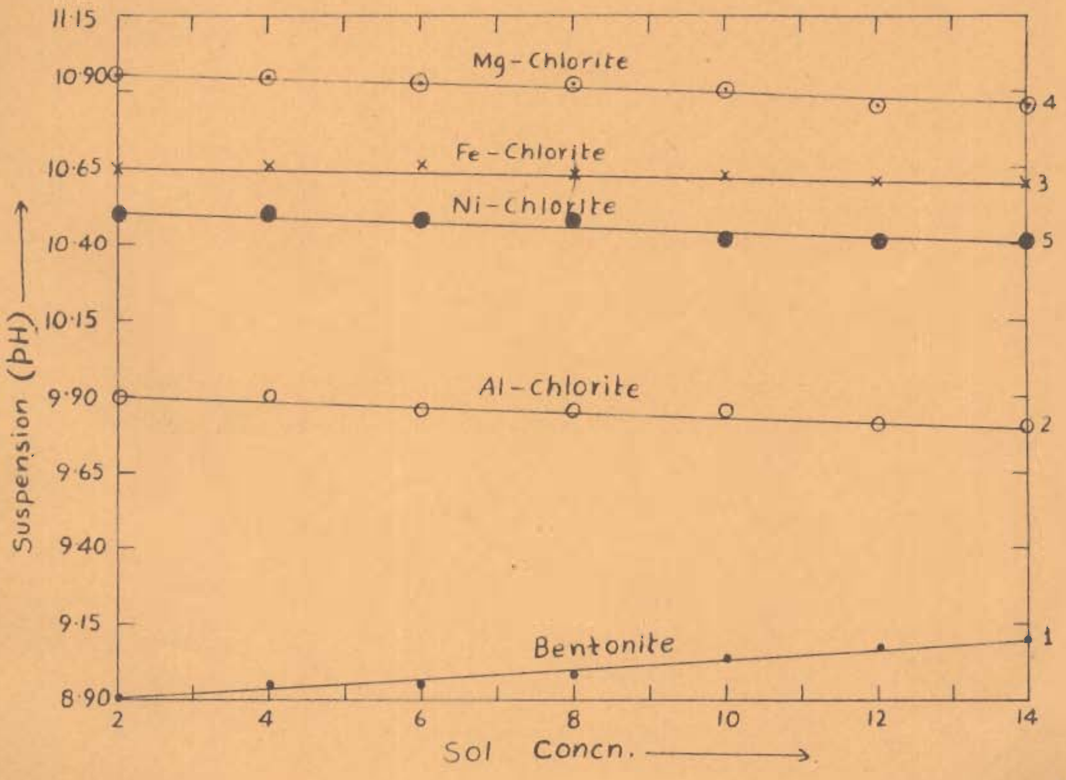


FIG. 4 (b)

SUSPENSION EFFECT IN AQUEOUS MEDIUM, ALKALINE RANGE, IN DIFFERENT CLAY MINERALS

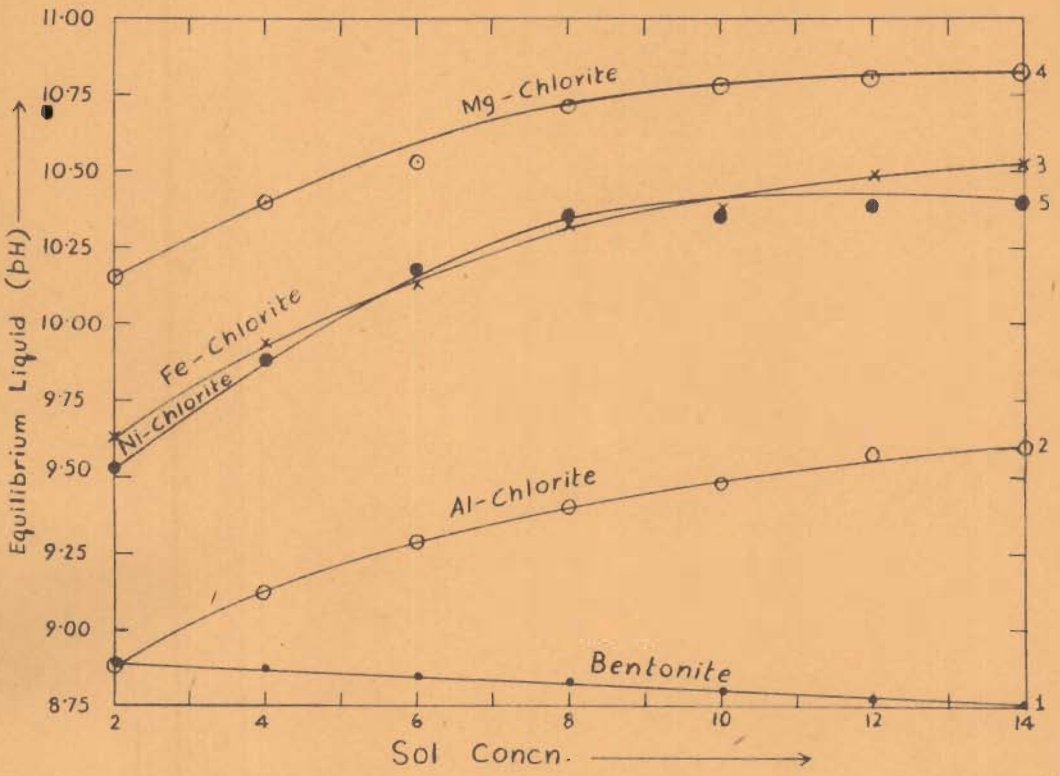


FIG · 4 (c)

SUSPENSION EFFECT IN ALCOHOLIC MEDIUM, ALKALINE RANGE, IN DIFFERENT CLAY MINERALS

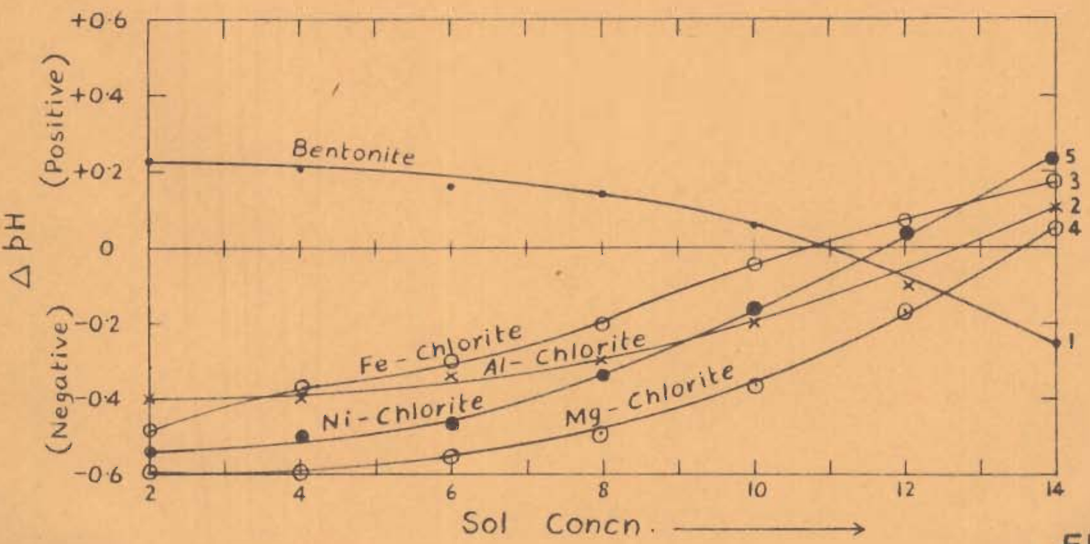
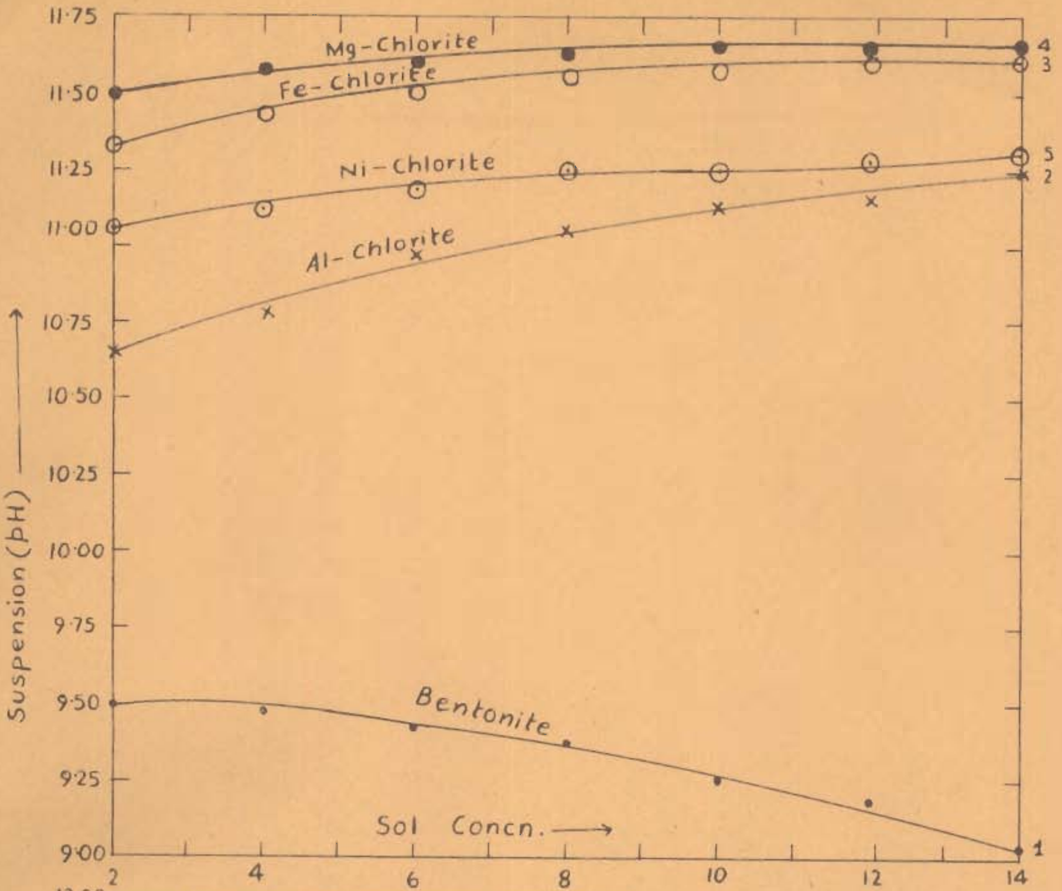
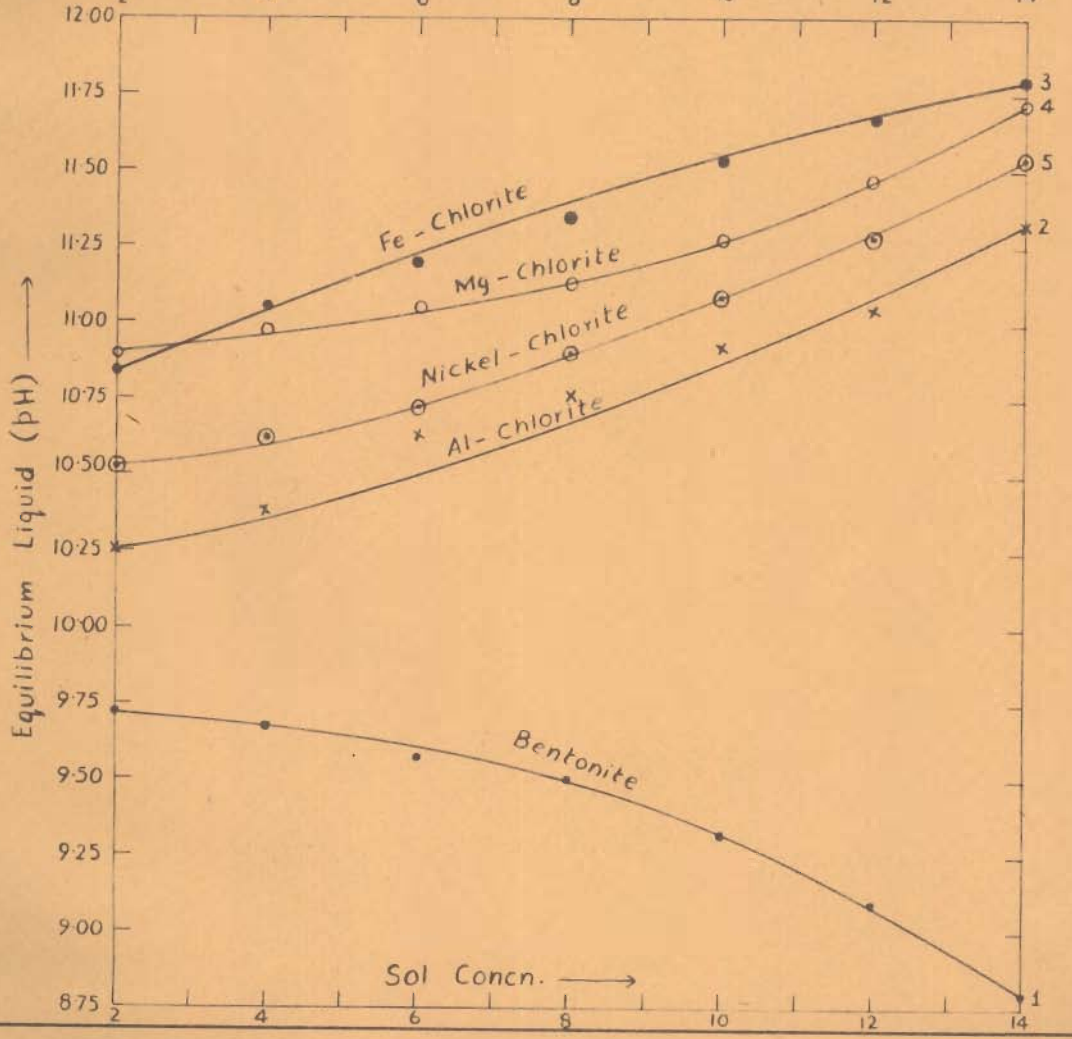


FIG · 5 (a)

SUSPENSION EFFECT IN ALCOHOLIC MEDIUM, ALKALINE RANGE, IN DIFFERENT CLAY MATERIALS



FIG·5(b)



FIG· 5 (C)

DISCUSSION

The results on sol concentration effect (Fig.1) for the bentonite clay and the four transformed clay structures (chlorites) reveal that the pH of the sols increases with increase in dilution. The nature of the plots, between concentration and pH values, (Fig.1), as well as the large similarity between the calculated and the observed pH values shows, that the Loosjes equation(131) is applicable, to systems under investigation. A similar behaviour was observed by Marshak (280) for montmorillonite, although, without emphasizing the importance of sol concentration effect in colloidal solutions. As pointed by Wiegner and Pallmann (129), this effect is mostly controlled by adsorbed ions in the double layer of the sol (both the diffuse and the Stern part); in the case of clays under discussion, these will be the H^+ ions for negatively charged inner layer. These observations are also in conformity with the conclusions of Peech et al.(141), in which the deflocculated clay suspensions, saturated with univalent cations (H^+ ions in this case), get short circuited by the saturated KCl of the salt bridge, resulting in a sharp potential drop across the diffuse double layer. This exaggerated ion activity, however, is reduced on dilution, due to lesser density of H^+ ions and falls off rapidly at extremely low concentrations. In view of the strong adsorption of H^+ ions, it is difficult to explain such variations simply on the basis of potential existing between the KCl bridge and the charged suspended particles, as proposed by Jenny et al. (140) and Overbeek (137).

On plotting the pH of the suspension (Fig.2 b), or the equilibrium liquid (Fig.2 c), against sol concentration, in aqueous medium, acidic range,almost similar curves are obtained for all the clay minerals investigated. The pH both of the suspension (Fig. 2 b) and the equilibrium liquid (Fig.2 c), decreases with increasing concentrations of the sol.

Interesting features leading to the identification, or at least differentiation, in the behaviour of bentonite and artificially transformed clay structures, are distinctly shown, when the pH differences between the suspension and the equilibrium liquid($\triangle$pH) are concerned. From these curves (Fig.2 a), it will be seen that in the case of bentonite, there is a regular fall in pH with increasing concentration of the sol, whereas while in the chlorite like structures a regular increase is observed.

The fact that the pH of the suspension is always lower than the equilibrium liquid, suggests that when the dispersed micelles settle out, the H^+ ions are adsorbed on the floccules, and the pH of the equilibrium liquid becomes larger, than that of the suspension. This behaviour is also explained in terms of what is called the"acid dispersing effect",(129).

Many new,interesting and informative points,emerge out, when these studies are carried out in the alcoholic medium. An entirely different behaviour is observed in the alcoholic medium, where variations in the pH values of the suspension (Fig. 3 b) and the supernatant liquid (Fig.3 c) are just the opposite of what are observed in the aqueous medium. This behaviour is further confirmed, from the plots of $\triangle$ pH versus clay concentration, (Fig.3 a). Here the curves, similar to those obtained in aqueous medium, for the four transformed clay structures, are obtained, only when negative $\triangle$ pH, instead of $\triangle$ pH, is plotted against clay concentration. Even with bentonite, the suspension effect, although not reversed, is greatly masked. The fact, that the adsorption of H^+ ions, controls these effects , is quite evident from these studies, since the adsorption of H^+ ions is appreciably decreased, in presence of alcohol. With transformed clay structures, negative adsorption sets in, most probably, due to the orientation adsorption of alcohol molecules on their particles.

Adsorption effects are not evident in suspensions, studied in the alkaline medium (Fig.4 a,b and c). This is not improbable, in view of the negative charge on the clay particles, which could result more in the peptization of the clay rather than its flocculation, resulting, eventually, in a very small suspension effect. It is, for this reason, that no pH variations are observed, at least with the transformed clay structures. With bentonite too, the variations in pH are not so marked as in the acid range. The small variations may be due to the well developed positive and negative electrical double layers in montmorillonite, as against the transformed varieties. The pH increases with sol concentration in case of supernatant liquid. This again points to the fact that the OH^- ions are not adsorbed on the double layer, but remain free in the dispersion medium. The plots of sol concentration against Δ pH are just the same, as for the corresponding alcoholic suspensions in the acid range.

The variations of pH in alcoholic medium for suspensions studied in the alkaline range (Fig. 5 a,b & c) show the same behaviour with regard to suspension effect and Δ pH-concentration relationship, with the only exception, that the variations in pH in the supernatant liquid are more marked than in the aqueous medium. This again supports the view point that the adsorption of ions in the electrical double layer is very much checked in presence of alcohol. The OH^- ions, which are likely to be adsorbed on the clay particles, however small their number may be, are not allowed to do so, in the alcoholic medium, with the result that the increase in pH with sol concentration becomes much larger, than observed in the corresponding supernatant liquid in the aqueous medium.

From the figures and this data it can be said that in no case the transformed clay structures behave like their parent original bentonite structure, as regards the suspension effect. This behaviour is just the reverse in these two clay structures and supports the view that a complete change-over from the bentonite structure takes place, on incorporating the hydrous oxide sols in the silica sheets of the montmorillonite unit. Also, these suspension effects, as observed in these cases, are different from those observed for kaolinite and illite, by Singhal and Malik, (143). It may further be added that although suspension effect can be profitably used to differentiate the various groups of clay minerals, from one another,like montmorillonite or kaolinite group of clay minerals,but it is not possible to differentiate between the different members of the same group of clay minerals,as in the case of these transformed bentonite structures,belonging to the chlorite family.

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CHAPTER V

Polarographic behaviour of the different clay minerals.

INTRODUCTION

Review of the earlier work:

Most of the polarographic studies, which have been undertaken since the invention of polarographic technique, concern with the reduction or oxidation of substances at the dropping mercury electrode (d.m.e.), in the form of true solutions, (281,282). Very few, if any, references are available on the polarographic behaviour of colloidal solutions. A somewhat different kind of depolarization of the d.m.e. by colloidal particles was described and explained by Majer (283), as a transport of positive charges of colloidal micelles to the cathode; however, the reduction of micelles seems to be more probable.

Very recently, Micka (284) has shown that the solid materials may also be determined by polarographic technique. The discovery of this phenomenon was made by him, (285), quite accidentally, while working with suspensions of active charcoal. Micka has further shown, (144,286, 287), that various insoluble substances, in the form of suspension, undergo direct reduction at the d.m.e.. These findings were confirmed, by a study of suspensions of carbon black, by Hallum and Drushel, (288).

Besides, attempts have been made to apply polarographic technique to problems of metallurgy (289 a), mineralogy and geology (289 b), though not with great success. Puri and Hoon (145) once, perhaps, in a bid to determine the c.e.c. of soils, took some current-voltage curves of soils, saturated with various cations and compared these polarograms with those obtained from the chlorides of the respective cations, drawing the close analogy between the two, but did not elaborate their findings. The behaviour of clay minerals, when subjected to this type of reduction, presents results of greater complexity and nothing has, so far, been reported which may indicate the utility of polarographic studies in clay suspensions.

Behaviour of precipitated oxides, sulphides etc.:

Micka (144) observed that in a suspension of heavy metal oxides, sulphides, selenides, tellurides, sulphur and selenium etc., which is kept stirred, contrary to the normal polarographic practice, by means of a stream of nitrogen bubbled through the polarographic cell, a relatively great reduction current flows through the cell, while in a quiet suspension no current is observed. It will not be out of place to mention that the function of stirring is not only to keep the particles suspended and to renew the surfaces near the d.m.e., but also to eliminate the diffusion current, as far as possible. Furthermore, he observed that current is a function of the potential of the d.m.e.. Hallum and Drushel (288) stated that chemisorbed oxygen, on the surface of carbon particles, was responsible for the current.

Micka has divided the substances, he investigated, into four classes. Firstly, suspensions of materials such as activated charcoal and oxides like manganese dioxide and cuprous oxide. These give irregular waves, which are not reproducible. Secondly, fresh precipitates such as sulphides of lead and mercury, which give good waves with a sharp and reproducible maxima. The third class consists of suspensions of substances like silver chloride and silver oxide, with which the current decreases on standing. Finally, the fourth class of substances includes insoluble materials like barium and lead sulphates, which give no current.

Recent work on suspensions:

In more recent work, Micka (290) has shown that the current, flowing during the production of the maxima, corresponds to the electrochemical reduction of the particles in suspensions. In case of carbon black, the current is either anodic or cathodic, depending upon the chemical treatment of the material. It is thus possible to distinguish between various types of carbon black. Kalvoda has made similar investigations using an oscillographic polarograph, (291).

Zagorski (292) has, also, carried out work with solid suspensions, connecting the dissolution rate of the suspension with its surface area.

Considerable fluctuations of the current are a characteristic feature of these current voltage curves and are given by the impacts per second of the particles with the electrode.

Kalvoda (291) has reported certain interesting observations, regarding the polarographic reduction of suspensions; (a) colour of the substance has a certain significance, (b) larger the radius of the cation the better the reducibility of the insoluble substance, (c) size of the insoluble particles also plays an important part.

Use of maxima suppressors:

Some of the maxima suppressors are known to enhance the polarographic maximas, as shown by von Stackelberg (293) and Weronski (294). Interpretation of a maxima, on current voltage curves, is one of the most difficult problems in polarography. Although, extensive theoratical and experimental studies have been carried out, by numerous investigators, there is no satisfactory theory to explain their effects.

Polarographic behaviour of aluminum, iron, nickel and cobalt when associated with complex systems:

The universal presence of iron and aluminum in all clay systems, might reasonably be assumed and the potentials can be interpreted in terms of the system, $Fe^{+3} + E \rightleftharpoons Fe^{+2}$, but Puri (12), from pH considerations, has ruled out the possibility of the role of this system, in oxidation reduction potentials of clays.

Aluminum ions are always liberated, in exchange with hydrogen ions, in H-clays and as such Al^{+3} ions are supposed to play some part in the polarographic behaviour of H-clays. Aluminum ions exist, in diluted aqueous solutions, with coordinated six molecules of water, thus forming a hexaquoaluminum ion, (295) , behaving like a weak acid, which explains many strange points in its polarographic behaviour, (296). Adsorption of aquoaluminum ions, at the d.m.e. surface, is evident from electro-capillary measurements, (297). Recently Heyrovsky (298) has shown in its polarographic behaviour that after the first maxima, there appears a second rounded maxima of catalytic nature, due to the occluded Al^{+3} ions in the $Al(OH)_3$ layers, formed by the successive loss of OH^- ions from the hexaquoaluminum ions as follows:

$$(Al\ (OH_2)_6)^{+3} \xrightarrow{3\ e} 3H + Al\ (OH)_3 + 3\ H_2O.$$

Cobalt and nickel ions are known to influence the catalytic maximas of very many proteins and amino acids, (299).

Supporting electrolyte in the polarography of clay suspensions:

The choice, of the proper supporting electrolyte, becomes an important factor, in studying the polarographic behaviour of clay suspensions, as these are very sensitive to any electrolyte (or even non electrolyte) additions. Even many uncharged surface active agents, like gelatin, coagulate the clay sols, if added in a higher concentration range.

Further scope of the work:

The polarography of hetrogeneous continuously changing systems is in its infancy and hope may be expressed that the refinement of this technique may lead to more general applications. It is, however, interesting to find that this polarographic technique, originally based upon diffusion in solution, has been shown to be capable of handling solid suspensions, proving the never ending versatility of this branch. The most sriking and important result is that substances of similar chemical composition, but of different crystallographic constitution, behave differently. The type of crystal lattice, comprising the structure of the suspension, influences its polarographic behaviour. Such distinction, without the aid of X-Ray diffraction analysis, has never been possible before. It would amount to the use of polarographic analysis, in hetrogeneous systems, as a means of distinguishing materials, with different crystallographic structures.

Aim of the present investigation:

From what has been reviewed above with regards to the differentiation of the various crystallographically different forms of hetrogeneous systems, by their polarographic analysis, it is evident, that currents other than the diffusion current play an important part, in their reduction at d.m.e.. The currents, mainly, to be counted are the adsorption and kinetic currents.

To estimate their role, with a view to find some means to distinguish the various types of clay minerals, on the basis of their polarographic behaviour, polarography of clay suspensions, both naturally occuring and modified structures and also the metal hydroxide sols, used in the preparation of these clays, was carried out, without the addition of any supporting electrolyte, in presence of various surfactants like gelatin, soaps and dye. More precise information is forthcoming by considering the influence of the mercury pressure and the imposed external resistance on these polarograms.

EXPERIMENTAL

Clay minerals used:

Bentonite, Kaolinte and Illite were imported through Martin and Harris, from the Ward's Natural Clay Corporation. Other clays used were the artificially transformed bentonite structures (chlorites), prepared as described in the previous chapters.

Preparation of clay sols:

The various clay sols were prepared (in hydrogen form) as described in the earlier chapters. The concentration of the sol was always kept constant. Great care was taken in the preparation of the sols, by centrifugation, as the change in particle size is known to shift the position of the maxima.

Surface active agents:

Solutions, with 10^{-3} M concentration, of gelatin (A.R., B.D.H.), methyl red (A.R., E.Merck), cationic soap (cetyl trimethyl ammonium bromide, Mol.Wt.364.0 approx., B.D.H.), anionic soap (sulphonated phenyl stearic acid, Mol.Wt. 440.0 approx.) and non ionic soap (lauric acid diethanolamine condensate, Mol.Wt.290.0 approx.), both laboratory prepared, in double distilled water, were used as the surfactants.

Apparatus:

Toshniwal's (India), battery operated, manual polarograph, type CLO-2, in conjuction with a sensitive Pye Scalamp Galvanometer in the outer circuit, was used for the work described. Nitrogen gas was used for the deaeration purposes. The H-type polarographic cell was thermostated at 30 ± 0.01°C. The capillary constant $m^{2/3}t^{1/6}$ was 2.985; drop time (open circuit) being 3.4 seconds. Saturated calomel electrode was used as the reference electrode.

Preparation of solutions:

20.0 ml. of the sol were mixed with the required amount of the surface active agent and the volume was made constant, in each case, by the addition of double distilled water. The solutions were kept well corked in pyrex boiling tubes for six hours to attain equilibrium.

Preparation of metal hydroxide sols:

Alumina and iron hydroxide sol were prepared, by the peptization of their respective hydroxides, the pH of these was adjusted with that of aluminum or ferric chlorite clay sol respectively.

Nickel and magnesium hydroxide sols could not be prepared in the acidic range. Nickel hydroxide sol was prepared by excessive washing of the nickel hydroxide precipitate,by the method of Tower and Cook(300).

Similarly, magnesium hydroxide sol was prepared, by the excessive washing of magnesium hydroxide, obtained by the precipitation of magnesium chloride with ammonium hydroxide. The magnesium hydroxide after excessive washing was taken up in boiling water and stabilized by the addition of some glycerol to it, which was further stabilized by keeping it with a mercury drop overnight.

The sols were analyzed by the method of Scott (301) for the respective oxides and the concentrations of the sols were adjusted to that present in the respective transformed clay structures.

Procedure for polarographic behaviour:

Polarograms were taken following the usual recommended procedure, (281, 282). Special care was taken for deaeration. Effect of the height of mercury column (results not given) and an external resistance, in the series (using a standard resistance box for the purpose), on these polarograms was also studied. Anodic waves of all the substances were also studied, but in no case, except ferric hydroxide sol, an anodic wave was realized, so the results are not shown. Also, the results of the addition of surfactants, to metal hydroxide sols, are not mentioned, as these were very similar to those observed in the case of chlorite sols.

REDUCTION OF BENTONITE SOL. AT d.m.e. IN PRESENCE OF SURFACTANTS

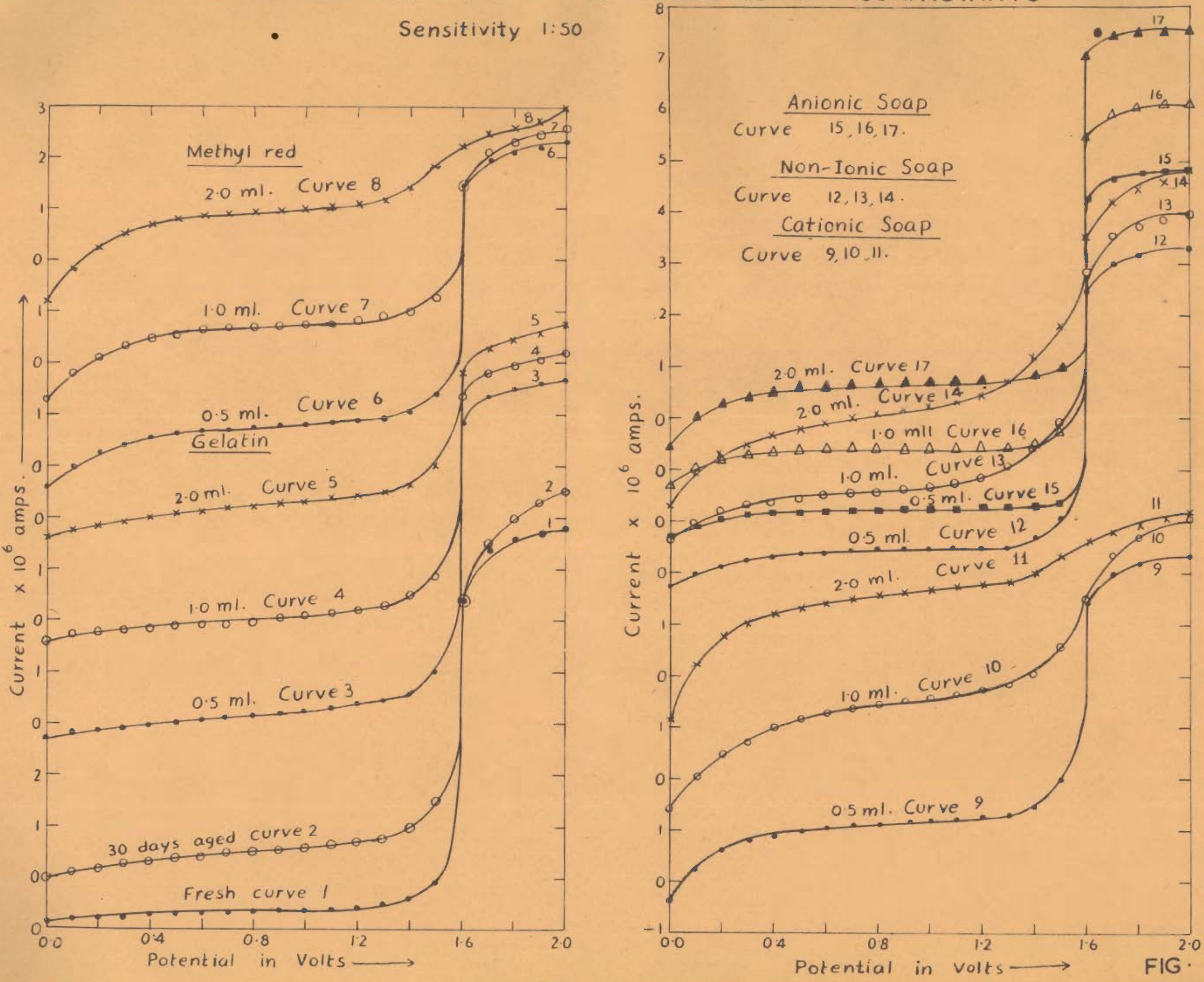

FIG. 1

REDUCTION OF KAOLINITE SOL. AT d.m.e. IN PRESENCE OF SURFACTANTS

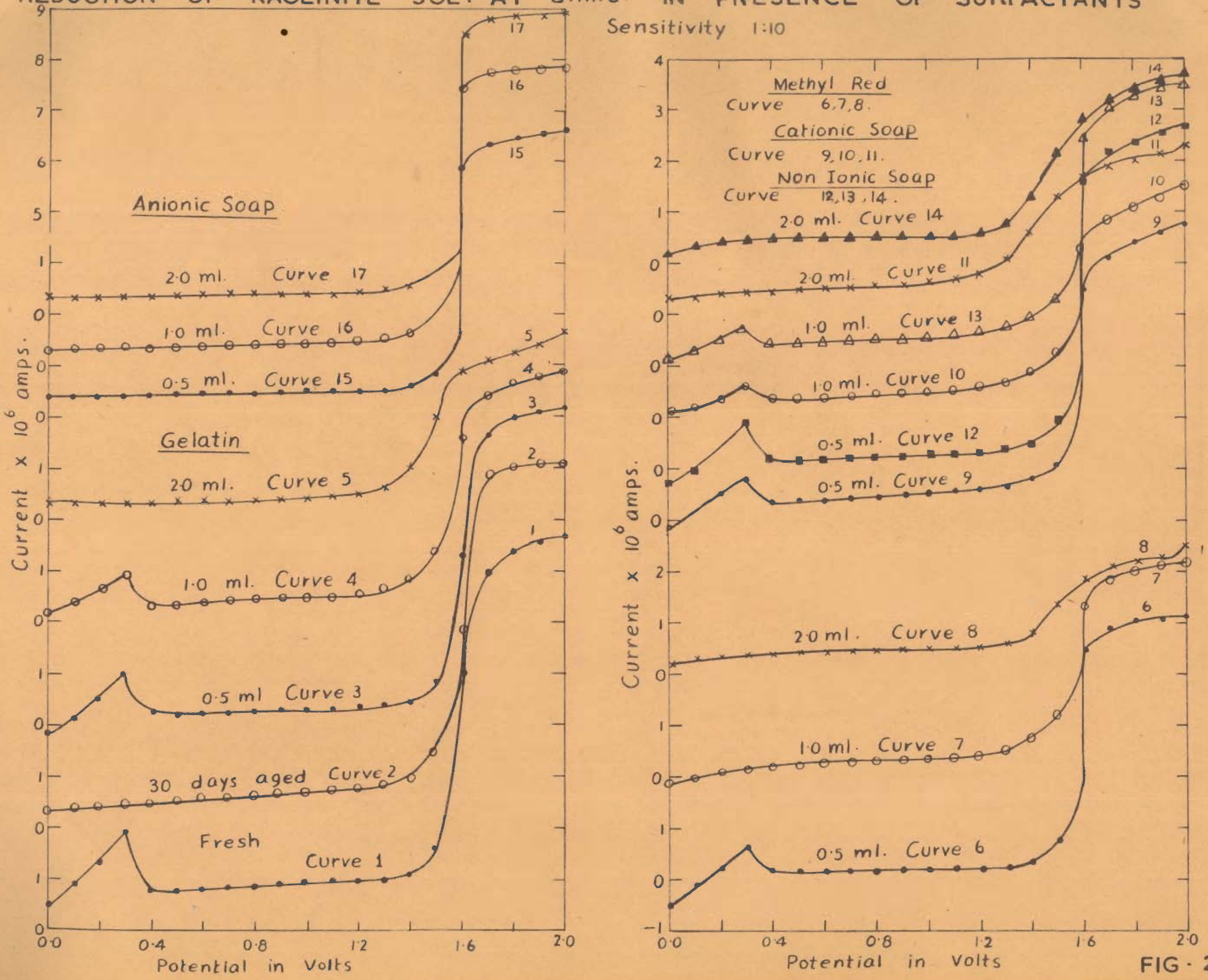

FIG · 2

REDUCTION OF ILLITE AT d.m.e. IN PRESENCE OF SURFACTANTS

Sensitivity 1:20

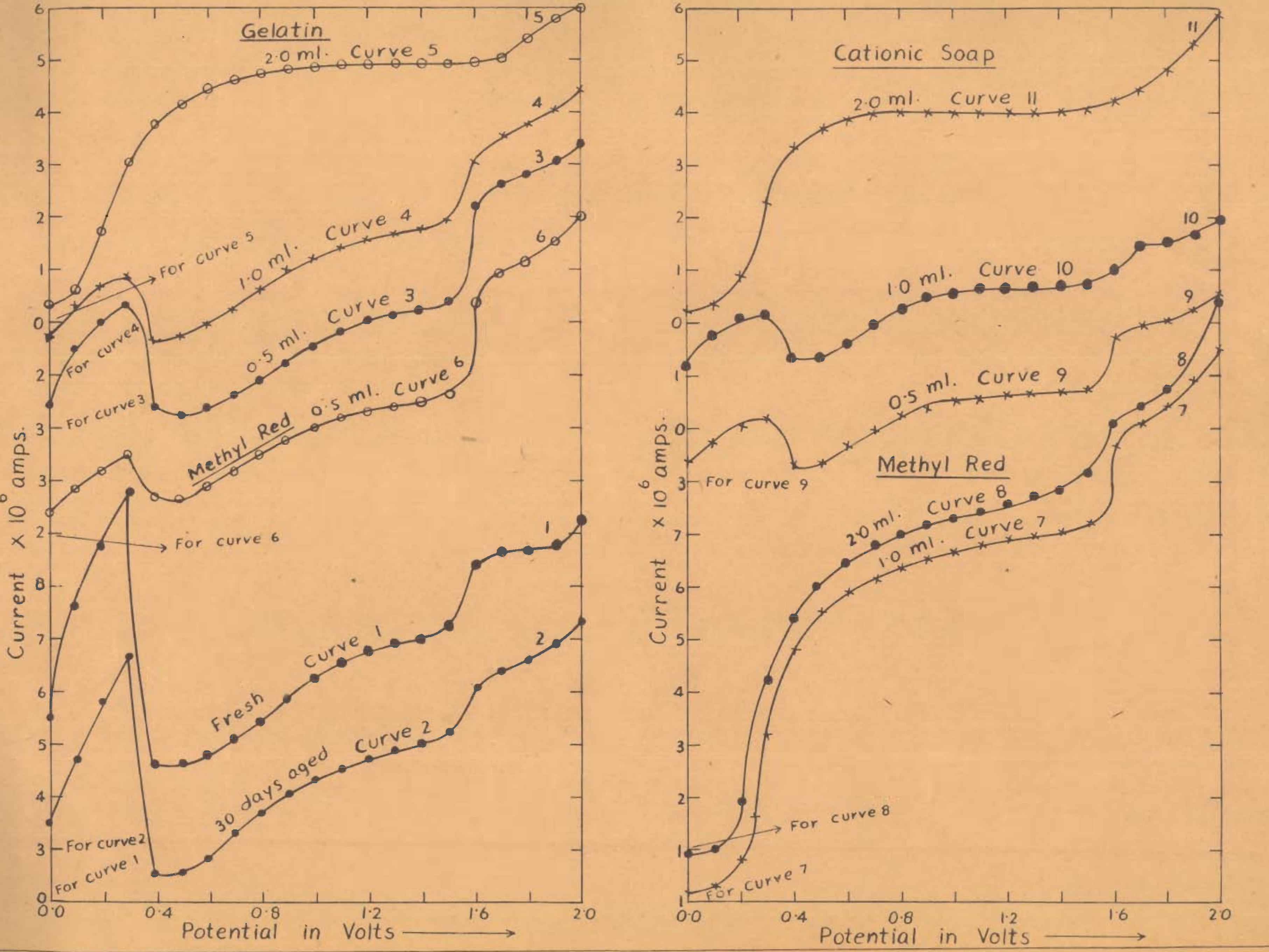

FIG · 3

REDUCTION OF ILLITE AT d·m·e. IN PRESENCE OF SURFACTANTS

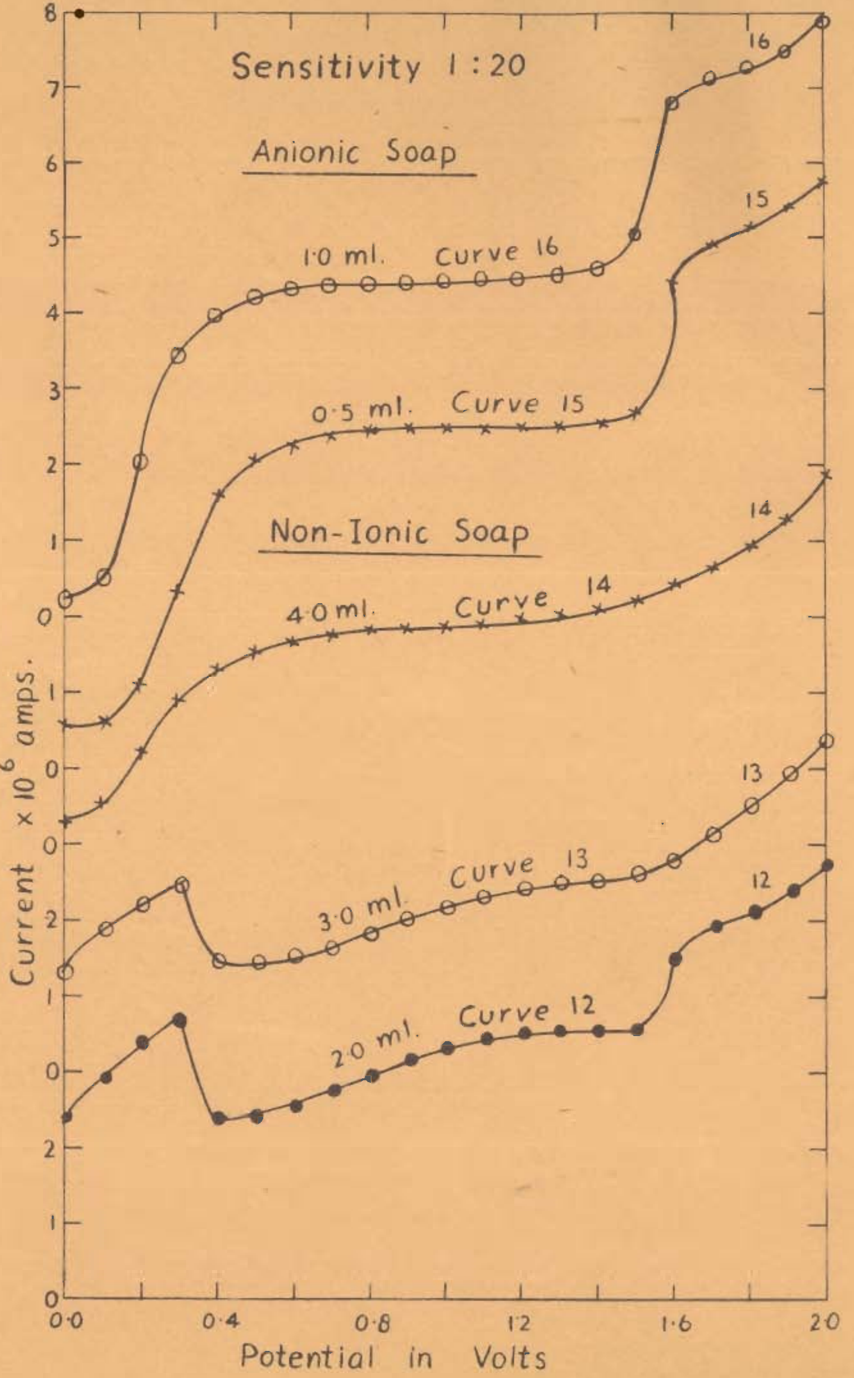

FIG. 3

REDUCTION OF Mg-CHLORITE SOL IN PRESENCE OF SURFACTANTS AT d.m.e.

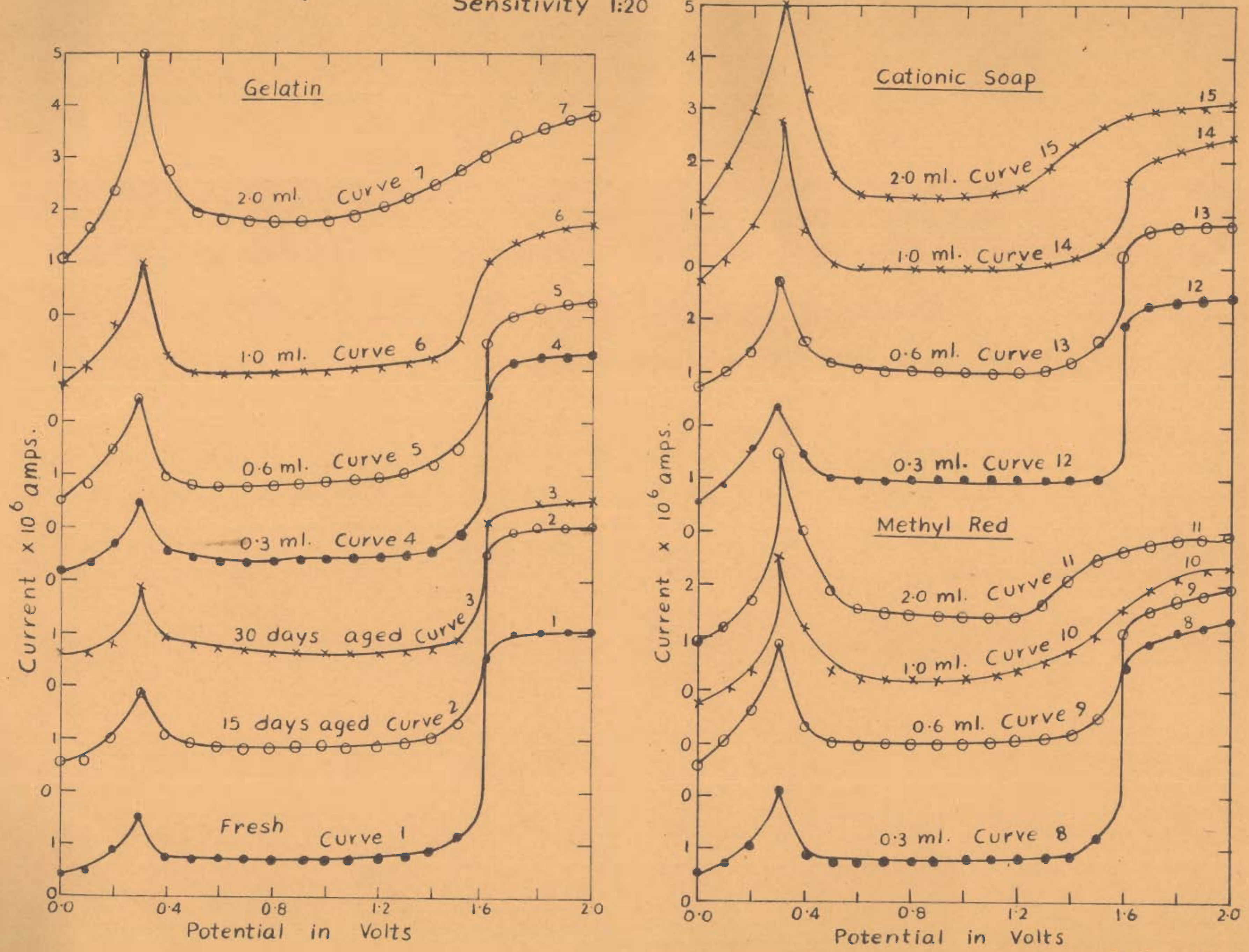
Sensitivity 1:20

FIG. 4

REDUCTION OF Mg-CHLORITE SOL IN PRESENCE OF SURFACTANTS
AT d.m.e.
Sensitivity 1:20

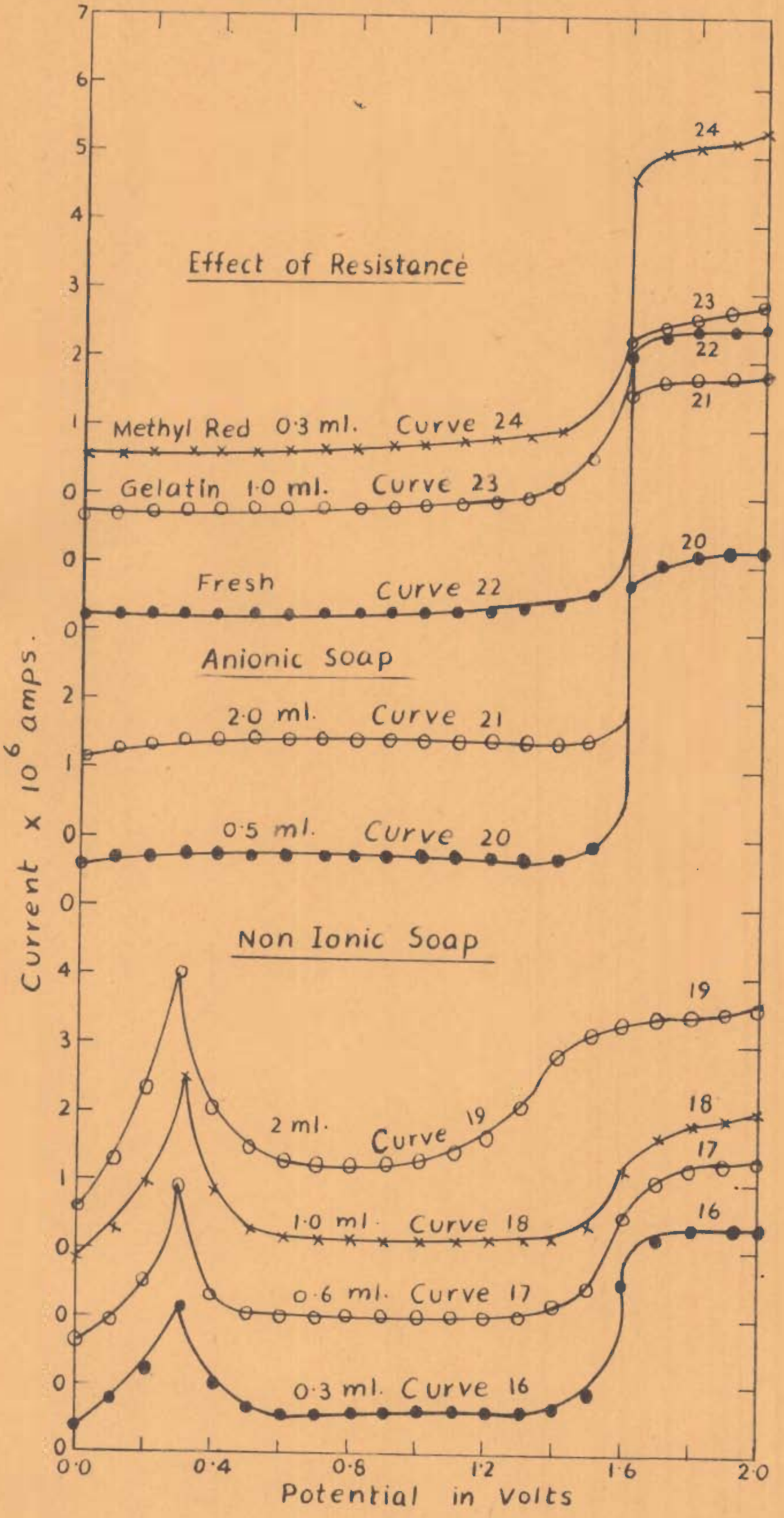

FIG. 4

REDUCTION OF Fe-CHLORITE AT d.m.e. IN PRESENCE OF SURFACTANTS

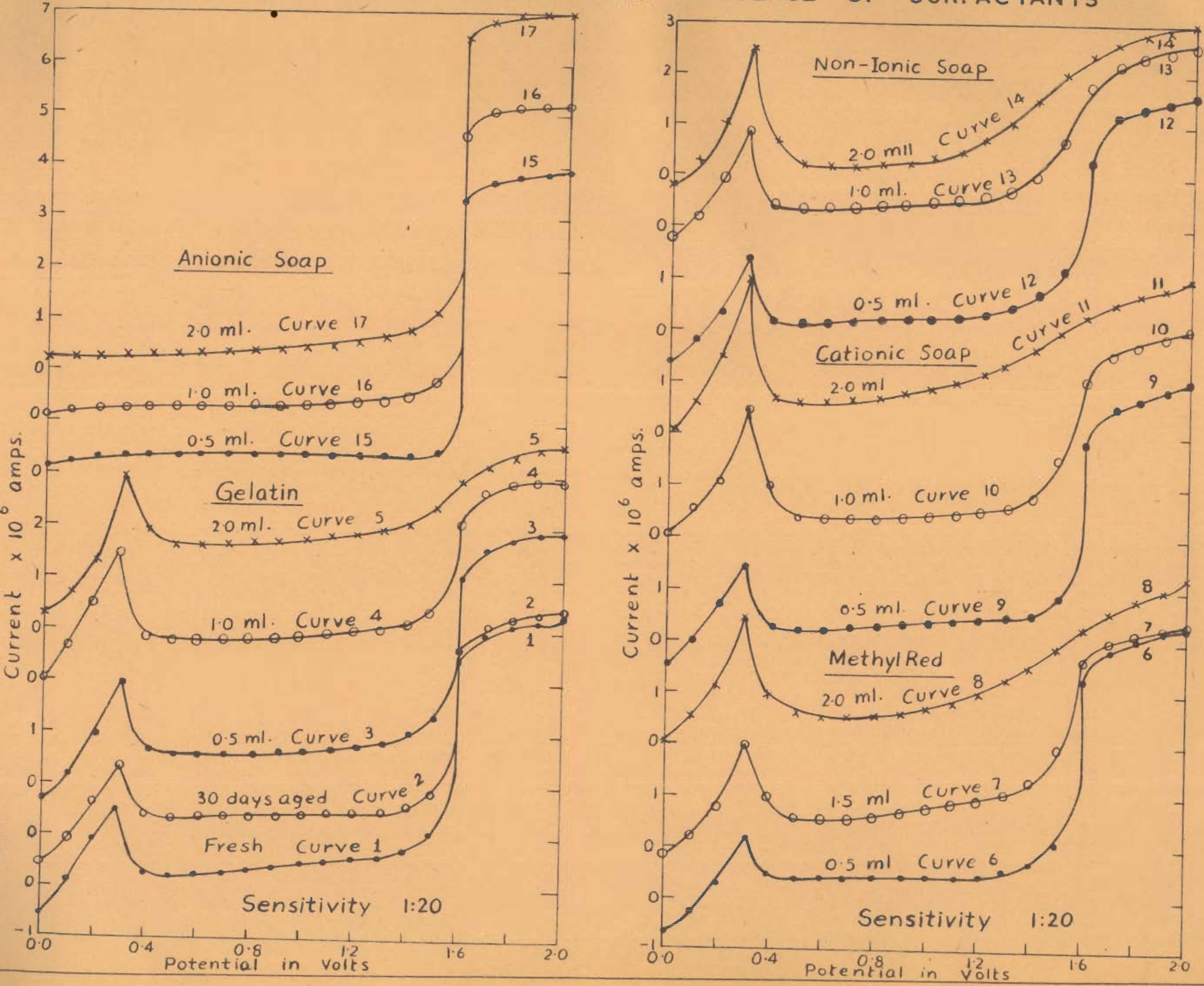

FIG. 5

REDUCTION OF Al-CHLORITE AT d.m.e. IN PRESENCE OF SURFACTANTS

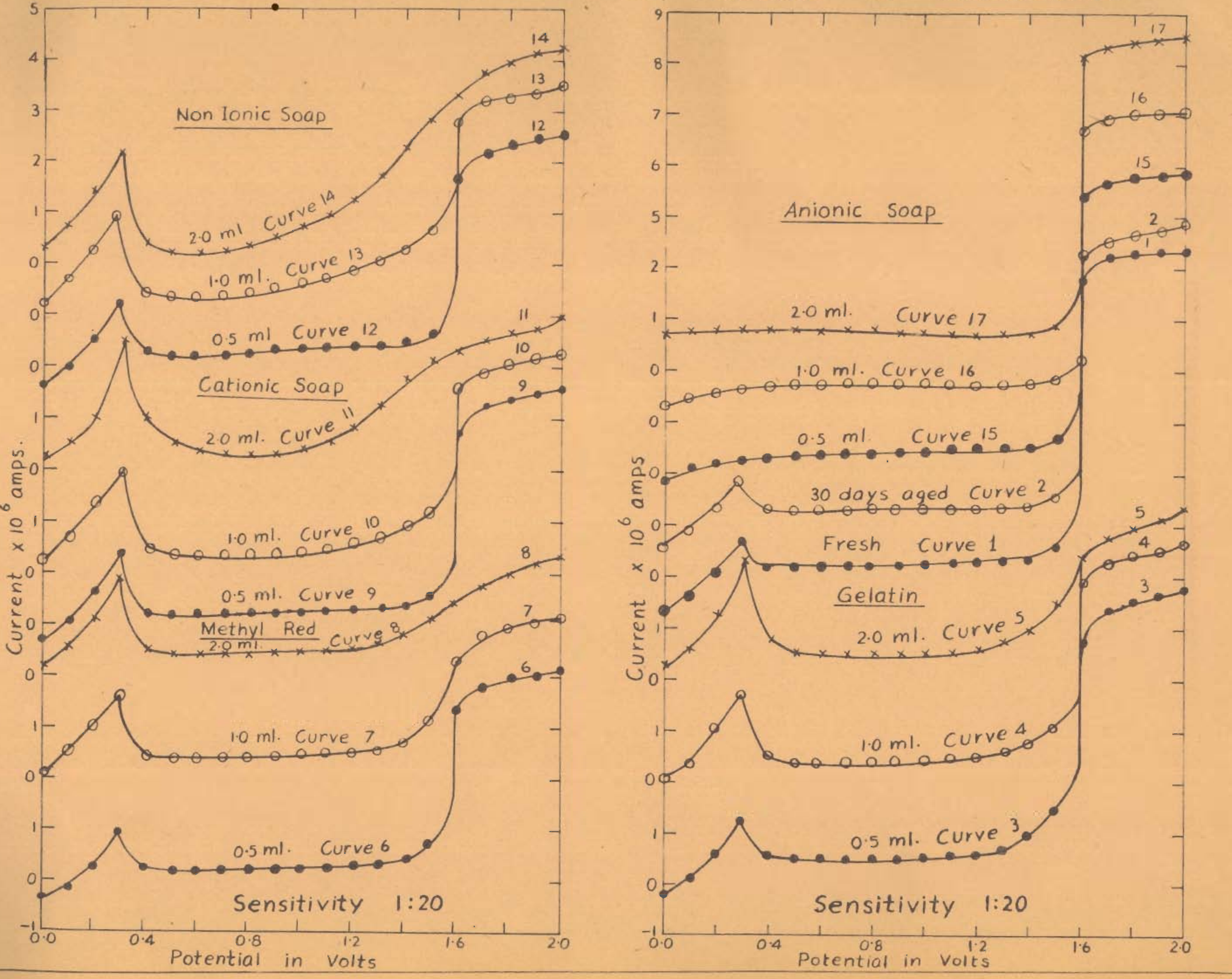

FIG. 6

REDUCTION OF Ni-CHLORITE AT d.m.e. IN PRESENCE OF SURFACTANTS

Sensitivity 1:10

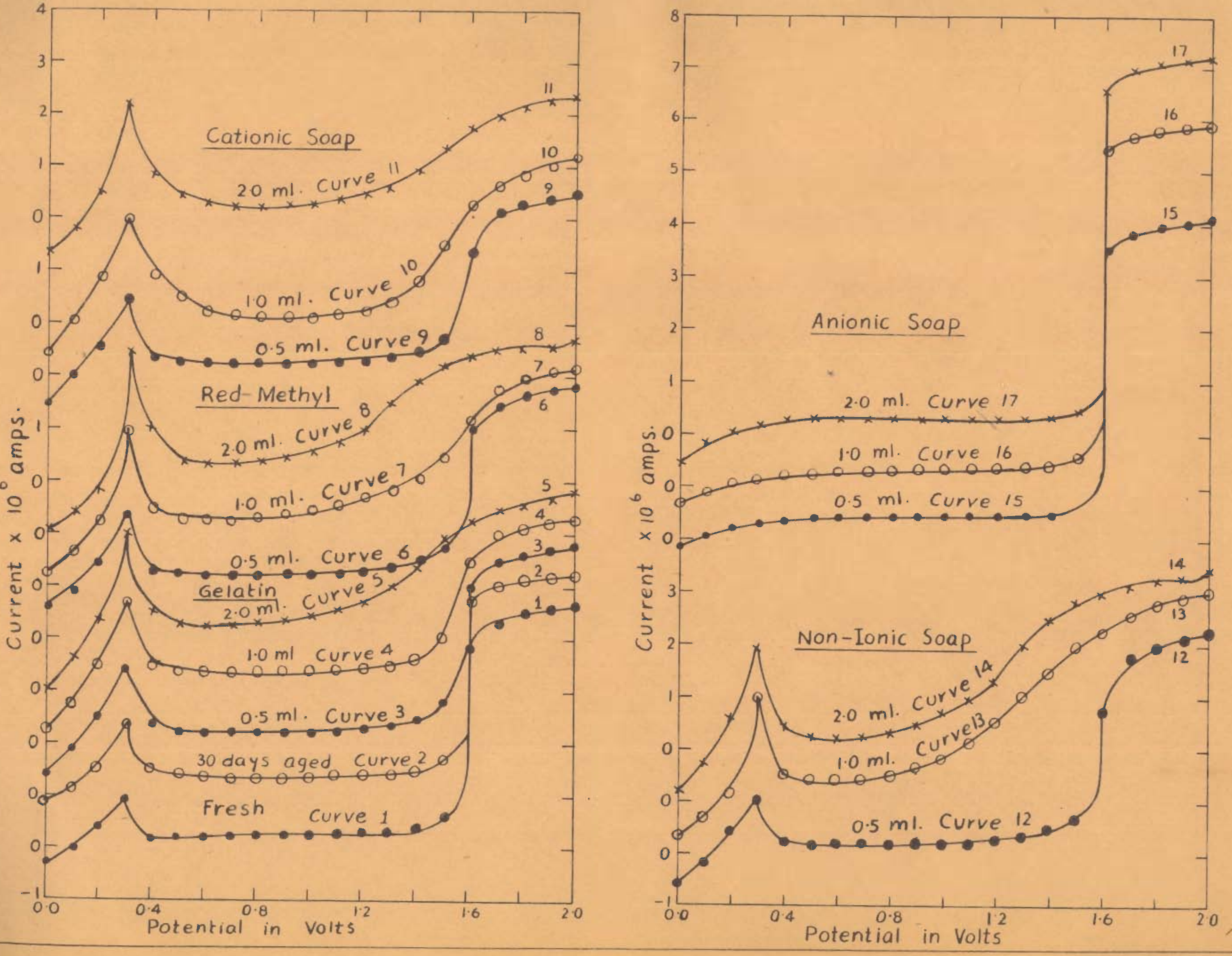

FIG. 7

REDUCTION OF METAL HYDROXIDES AT d.m.e.

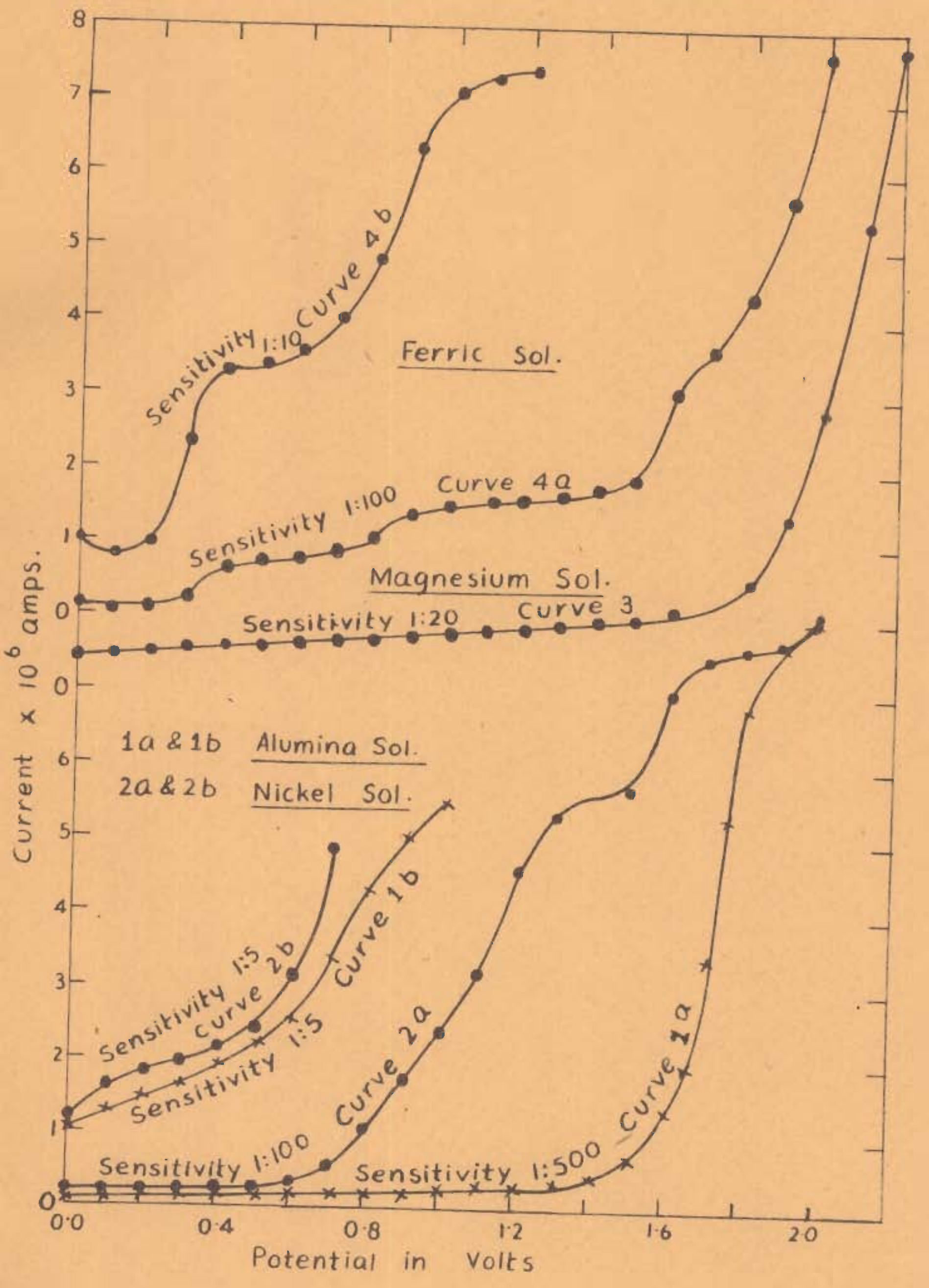

FIG. 8

RESULTS

1. Reduction of bentonite clay sol at d.m.e.: (Fig.1).

(i) No kink or maxima appears both in the fresh(curve 1) or aged (curve 2) sol.

(ii) No maxima appears, either with gelatin(curves 3-5), methyl red (curves 6-8), cationic soap(curves 9-11), non ionic soap (curves 12-14), or anionic soap (curves 15-17) at any concentration of these surface active agents.

(iii) A hydrogen (or more precisely H-Al) wave, well defined in nature, is realized with $E_{1/2} = -1.6$ V. with ageing of the sol there is a slight decrease in the hydrogen wave height.

(iv) The original hydrogen wave height decreases with increasing concentration of these surfactants (curves 3-14) and finally vanishes; except in the case of the addition of anionic soap (curves 15-17) which results in the increase of the height of this wave.

2. Reduction of kaolinite clay sol at d.m.e.:(Fig.2).

(i) A kink or maxima appears at -0.3 V in the fresh sol (curve 1) but does not persist on ageing (curve 2).

(ii) With increasing concentrations of the surfactants, like gelatin (curves 3-5), methyl red(curves 6-8), cationic soap (curves 9-11),nonionic soap(curves 12-14), and anionic soap(curves 15-17) the maxima height decreases and finally vanishes.

(iii) A hydrogen wave,well defined in nature,is realized with $E_{1/2} = -1.6$ V. The hydrogen wave height remains unaffected on ageing.

(iv) Same as observation No.(iv) in the case of bentonite clay sol.

3. <u>Reduction of illite clay sol at d.m.e.</u>: (Fig.3).

(i) A kink or maxima appears at -0.3 V in the fresh(curve 1) sol and persists even on ageing (curve 2).

(ii) With increasing concentration of the surfactants, like gelatin(curves 3-5), methyl red (curves 6-8), cationic soap(curves 9-11), nonionic soap (curves 12-14),and anionic soap (curves 15-16) the height of the maxima decrease till it vanishes but gives rise to another polarographic wave in its place.

(iii) A hydrogen wave, well defined in nature, is realized with $E_{1/2} = -1.6$V.The hydrogen wave height decreases on ageing.

(iv) Same as observation No.(iv) in the case of bentonite and kaolinite clay sols.

4. <u>Reduction of magnesium chlorite clay sol at d.m.e.</u>: (Fig.4).

(i) A kink or maxima at -0.3 V appears in the fresh (curve 1) sol which persists even on ageing (curves 2-3).

(ii) This maxima persists at all concentrations of the surfactants, like gelatin (curves 4-7), methyl red (curves 8-11), cationic soap (curves 12-15) and nonionic soap (curves 16-19). The height of the maxima increases with the increase in the concentration of the surfactants, but not linearly.

(iii) With anionic soap (curves 20,21) the maxima disappears.

(iv) A well defined hydrogen wave is observed with $E_{1/2} = -1.6V$. On ageing the sol the hydrogen wave height continuously decreases.

(v) Same as observation No.(iv) in the previous cases.

(vi) When an external resistance, greater than that of the cell solution, is added in series, in the outer circuit, all these maximas disappear (curves 22-24).

5. Reduction of ferric chlorite, aluminum chlorite and nickel chlorite clay sols at d.m.e.: (Figs. 5,6 and 7, respectively).

All these three clay sols behave exactly in a similar fashion, as does the magnesium chlorite clay sol, mentioned above.

6. Reduction of metal hydroxide sols at d.m.e.: (Fig. 8).

(a) Aluminum hydroxide sol:- (Curve 1).

(i) No maxima or kink appears in the fresh sol.

(ii) A mixed, ill defined, H-Al wave appears with $E_{1/2} = -1.65$ V.

(iii) The height of this mixed wave decreases with the increase in concentration of the surfactant added except anionic soap addition, where the height increases with the concentration of the soap.

(b) Ferric hydroxide sol:- (Curve 4).

(i) Small kinks at -0.1 V and + 0.1 V appear in the cathodic and anodic waves respectively.

(ii) Waves with $E_{1/2}$ at -0.3, -0.85 and -1.58 V appear in the cathodic reduction; for anodic oxidation a wave appears at + 0.45 V, $E_{1/2}$ value.

(iii) Kinks and the waves with $E_{1/2}$s - 0.3 and -1.58V disappear on the addition of surfactants, except in the case of anionic soap additions, where the kinks disappear but the wave with $E_{1/2}$ -1.58 V increases in height.

(c) Magnesium hydroxide sol:-(Curve 3).

(i) Highly ill defined wave, without any kink or maxima, is observed in the potential range -1.4 V to -2.2 V.

(ii) Surfactants tend to refine the nature of this wave and shift the approximate value of $E_{1/2}$ to positive side.

(d) Nickel hydroxide sol:- (Curve 2).

(i) No kink or maxima appears in the fresh sol.

(ii) Two waves with $E_{1/2}$s -1.05 V and -1.58V are observed.

(iii) The height of the second wave decreases with an increase in the concentration of the surfactants, except in the case of anionic soap where the height of this wave increases with the increase in concentration of the soap.

DISCUSSION

There are two striking features of the reduction of various clay minerals, including the transformed clay structurers, at the d.m.e.. These are the appearence of well defined polarographic reduction wave, with $E_{1/2}$ = -1.6 V and the existence of kinks or maximas (except in case of bentonite) at -0.3 V, and the absence of any high migration currents, even in the absence of any supporting electrolyte.

Nature of the reduction wave:

The polarographic wave, with $E_{1/2}$ = -1.6 V, can be the hydrogen wave. Since the $E_{1/2}$ for the reduction of aluminum ions, at d.m.e., also lies near this potential, the possibility of a mixed wave, due to the simultaneous reduction of H^+ and Al^{+3} ions, cannot be ruled out.

The fact that the height of these waves decreases on ageing (for all clay minerals except kaolinte), may be taken as an indication of the existence of the mixed waves. It appears that on ageing replacement of H^+ by Al^{+3} ions takes place, resulting in lowering of the diffusion current, due to lower diffusability of Al^{+3} ions. Since replacement of this type will be very small in two layer clay minerals, very little change in the hydrogen wave height is observed in kaolinite, on ageing.

Distortion of the waves takes place, on addition of maximum suppressors, like gelatin, methyl red, cationic and nonionic surfactants and in case of bentonite and the artificially transformed clay structures, the wave completely vanishes. Anionic surfactant(sulphonated phenyl stearic acid) used here, is expected to give a hydrogen wave, on reduction and addition of this surfactant should increase the height of the hydrogen wave,instead of bringing about its distortion or complete annihilation. This is what has actually been observed.

Nature of the kink or maxima:

Except for bentonite, kinks or maximas appear at -0.3 V, in the polarograms of all the clay minerals investigated. Inspite of the fact that they appear at the same potential their behaviour differs from clay to clay. Thus for chlorites and illite these persist even on ageing, whereas in the case of kaolinite these disappear under similar conditions.

Addition of maxima suppressors or surfactants throws more interesting light on the nature of these kinks. The height of the kinks is highly suppressed or these completely disappear by the addition of surfactants, in the case of kaolinite and illite. Moreover, it results in the emergence of a new polarographic wave in place of the maxima in the case of illite. But the behaviour is altogether different with the artificially prepared chlorite structures, where the addition of these substances(except anionic soap) brings about an increase in the height of the maxima or kink, although this increase is not linearly dependant on the concentration of the surfactant.

Based on several considerations, it can be concluded that these kinks or maximas are not the ordinary electrocapillary maximas, associated with diffusion currents. Had it been so, addition of gelatin, methyl red and some other surfactants etc., would not have resulted simply in the suppression or complete annihilation of the wave, but in the appearance of a well defined polarographic wave, like that associated with the reduction of metal ions. Moreover, the existence of the maxima should not be dependant on the age of the sol and should persist in fresh as well as aged sols. The fact that the kink or maxima persists on ageing in some clay sols and not in others goes to show that these are not similar to the ordinary maximas of the first or the second type, usually met with in reduction waves.

From what has been said above, it may be concluded that the existence of the kinks or maximas, is highly dependant on the physical state, (type of the crystal lattice, size and shape of the colloidal micelle and surface area etc.), of the clay and not on the chemical constituents, of which the clay is made of.

Having decided that the kinks or maximas are not the ones associated with diffusion currents, it is to be assessed whether their existence is due to adsorption or catalytic currents or both.

It is well known, that when some form of polarographically active substance is adsorbed at the d.m.e., then in such cases two waves are obtained, one of which corresponds to the reduction or oxidation of the free form of the substance and the second is that of its adsorbed state. Here it appears, that the kinks or maximas, are due to the adsorption of the clay on the mercury drops and the second wave is due to the reduction of hydrogen or hydrogen plus aluminum, (211). Ageing of the sol can bring about agglomeration of the particles, thereby reducing their surface active properties. This would, subsequently, result in lesser adsorption of the particles on the d.m.e.. Disappearance of the kinks or maximas on ageing, in case of kaolinite, may be due to this fact. That bentonite does not show any kinks or maximas in its reduction waves may be taken as an indication of the fact that bentonite is less capillary active than the other clay minerals.

Further support of the fact that the kinks or maximas do not form a part of the diffusion current, is forthcoming from the fact that insertion of outside resistance, considerably reduces or even leads to disappearance of the height of these maximas or kinks. The results are in complete agreement with the observations of Bridicka (302), who found that prominent maximas(kinks) are greatly suppressed, by inserting a high resistance in series.

Behaviour of kinks or maximas in presence of surfactants:

In all clay minerals, except the artificially prepared chlorite structures, the maximas are suppressed on the addition of surfactants. This behaviour is a normal one, since the addition of the surfactants would considerably reduce the adsorption of clay particles on the d.m.e., thereby reducing the magnitude of the adsorption current.

That no kink or maxima appears in presence of anionic surfactant, in case of even the chlorite like structures, points to the fact that the mercury drop is positively charged. It is quite probable if we assume that the H-clay complex dissociates as follows:

$$\text{H- clay} = H^{+} + (\text{clay})^{-}.$$

The clay anion would now be adsorbed on the mercury drop and with the flow of electrons in the inner mercury layers, (282), the mercury surface will, eventually, become positively charged. The diffusion of anionic soap will, now, be very much accelerated towards the positively charged mercury surface and the clay anions would get very little opportunity to be adsorbed on the mercury drop. A kink or maxima would, therefore, not appear. Moreover, since the kinks appear at a less negative potential(-0.3 V) than the electrocapillary maximum potential(-0.56 V) it will further promote adsorption of the anions of the soap.

Reduction of metal hydrous oxide sols at the d.m.e.:

Micka (loc. cit.) has studied the behaviour of suspensions(precipitated oxides, sulphides etc.),at the d.m.e. and according to him the production of the maxima corresponds to the electro-chemical reduction of the particles, of the suspension, and that it is only possible, if adsorption forces exist between the mercury electrode and the suspension. At a certain potential these adsorption forces reach a maximum value and a maxima in current-voltage curves is realized. The acute maxima, observed between -1.5 V and -1.7 V, against a calomel electrode, with suspensions of ferric, cobalt and nickel sulphides, in an ammonium salt, has been explained, due to the reduction, corresponding to the following reaction mechanism scheme:

$$\begin{aligned} MeS + 2e &= Me^{+} + S^{--} \\ S^{--} + 2\,NH_4^{+} &= H_2S + 2\,NH_3 \\ Me + H_2S &= MeS + H_2 \,, \end{aligned}$$

the intensity of the current depending upon the ageing of the sol. Moreover, the coagulation time is interpreted as the time between the formation of the sol and the rise of the catalytic current. The decrease in the current of silver oxide on standing is attributed to the alteration of the state of the particles and surface area due to ageing.

From what has been said above, on the basis of the large amount of work done, (144,283-288,291,292), it can be said that a number of factors control the reduction of suspensions. These are: (i) adsorption, (ii) catalytic effects, (iii) radius of the cation, (iv) size and shape of the particles and their surface area etc.. Recognition of these factors, singly or combined, should be taken into account when explaining the reduction of suspensions, irrespective of the fact, whether these are hydrophobic sols, clay sols or suspensions of silica or carbon.

The reduction waves of the metal hydroxides (Ni^{++}, Mg^{++}, Fe^{+3} and Al^{+3}), used in obtaining artificially prepared chlorite structures, do not give kinks, (except for ferric hydroxide, where small kinks at -0.1V and + 0.1 V, probably due to the solubilized oxygen, (282), or ill defined waves, with $E_{1/2}S$ = - 0.3 and -0.85 V are realized), or pronounced maximas, as in the case of clay minerals. Hydrogen wave is obtained in these cases, except magnesium hydroxide sol, which was not prepared in the acidic medium. The effect of the addition of the surfactants, on the hydrogen wave, is just the same as in the case of clay suspensions viz., deformation of hydrogen wave and its subsequent disappearance, with increasing amount of the surfactants, except the anionic soaps, in which case the hydrogen wave height increases with the increase in the concentration of the soap.

With magnesium hydroxide sol the behaviour is different. Here ill defined waves, without any maxima, are observed in the potential range -1.4 V to -2.2 V. Moreover, the addition of surfactants tends to refine these waves and shifts the $E_{1/2}$ value towards more positive potentials.

Maxima of artificially prepared chlorites in presence of surfactants other than anionic soap:

The chlorite samples do not contain free metal hydroxide, otherwise, possibly, no kink or maxima would have appeared. Similarly the original bentonite structure does not exist in these samples. Appearance of kinks, accompanied with increase in wave height in presence of maximum suppressors, reveals that the original clay structure has been transformed and we are, now, dealing with the reduction waves not connected with either of the naturally occuring clay minerals.

Why transformation into a chlorite like structure brings about an exaltation of the maxima, in presence of the maxima suppressors and surfactants, is not easy to explain. It may, however, be said that the introduction of the metal hydrous oxide, in between the silica layers, catalyses the adsorption phenomenon on the mercury drop, with the result that together with the adsorption current, catalytic current also appears. It is not unlikely that the surfactants and maxima suppressors instead of checking the adsorption of clay particles get adsorbed on the clay particles themselves and are subsequently reduced, which will result in the enhancement of the current.

Polarographic identification of clay minerals:

The table given on the next page provides the necessary information for distinguishing between different clay minerals in their hydrogen form.

Table for the identification of clay minerals on the basis of their polarographic behaviour.

Clay mineral.	Position of the kink.	Effect of surfactants on the kink.	Effect of ageing on the kink.	Position of H-wave $E_{1/2}$.	Effect of surfactants (except anionic soap) on H-wave.	Effect of anionic soap on H-wave.	Effect of ageing on H-wave height.
Bentonite.	No kink.	-	-	-1.6 V.	Suppression of its height.	increase in height.	Decreases.
Kaolinte.	-0.3 V.	Vanishes.	Vanishes.	-do-	-do-	-do-	Negligible decrease.
Illite.	-do-	Vanishes but a wave appears in its place.	Persists.	-do-	-do-	-do-	Decreases.
Chlorites. (transformed bentonite structures).	-do-	Increase in its height.	-do-	-do-	-do-	-do-	-do-

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Artificially prepared chlorite structures have been realized in two ways: (i) working at high temperatures and pressures, (ii) introducing the metal hydrous oxide in the unit sheets of montmorillonites, at ordinary temperature and pressure. In the former field, valuable contributions have been made by Noll, Roy and Gruner etc., (pp.3-4), but not much has been done in the case of structures formed by the latter method, especially from the view point of their identification and characterization. The work of Aleshin, Barshad, Caillere and Henin, Longuet-Escard, Youell, and Slaughter and Milne etc., (pp.4-6), although limited to the preparation of these structures, may be taken as a step in the right direction for solving the intricacies existing in the minerals. Besides, a knowledge of their physico-chemical behaviour is important for geologists and others dealing with sedimentary rock material or the clay colloid chemists.

Investigations on chlorite structures, obtained from metal hydrous oxides, become all the more interesting when viewed from the colloid-chemical stand point, since these involve not only clay fractions but hydrophobic colloidal systems, artificially interwoven into the naturally occuring colloid material which itself is rarely hydrophobic in character.

Based on the considerations enumerated above, the work described here was undertaken. It was felt that a satisfactory solution of the problem was possible if studied under the following heads:

(i) preparation of magnesium, aluminum, nickel and iron chlorites, (p.42),

(ii) ensuring the realization of artificial structures, by comparison with the already existing X-Ray data; this has been possible only in the case of magnesium and aluminum chlorite for which X-Ray data is available, (pp.73-76),

(iii) X-Ray Diffraction, Differential Thermal Analysis, Dehydration Curves, Infra Red Spectrophotometric Analysis, Chemical Analysis, Cation Exchange studies on magnesium, aluminum, nickel and iron chlorites, and interpretation of the data, wherever possible, in the light of the available information, (pp.33-76),

(iv) potentiometric and conductimetric titrations of these structures, including a study of the Wiegner Pallmann Suspension Effect, (pp.77-107), (pp.148-169),

(v) viscometric studies on the above mentioned chlorites and the possible use of the viscosity data in identifying them, (like the earlier studies carried out by Singhal and Malik, on naturally occuring clay minerals and soil samples; these were found useful in identifying these artificial structures), (pp.108-147),

(vi) polarographic reduction of the hydrogen form of the various naturally occuring and artificially transformed clay suspensions: an approach likely to give results of far reaching importance if extensively employed, (pp.170-193).

1. **Preparation of chlorite structures by transformation of the montmorillonite structure**: (p.42).

The method recommended by Slaughter and Milne has been followed for the preparation of artificial chlorites, by precipitating a 2N solution of the metal chloride in a concentrated (6%) bentonite suspension, kept stirred at a high speed with a magnetic stirrer, using ammonium hydroxide as the precipitant. After complete precipitation, and washing with alcohol water mixture, the complex so obtained is dried at 105°C and aged for three months.

2. **X-Ray Diffraction studies**: (pp.49-50,58-60,73-76).

The X-Ray diffraction analysis of magnesium and aluminum chlorite is in full conformity with the data given by Slaughter and Milne for their products, but many new interesting and informative points emerge from the X-Ray diffraction studies of the nickel and iron chlorites formed in this way, contrary to the observations of Slaughter and Milne, that iron chlorite cannot be identified by X-Ray diffraction. It was found that both nickel and iron hydroxide-montmorillonite complexes (heated as well as unheated samples) give X-Ray patterns, conforming to those for chlorite structures. Well defined peaks at 14.6 and 15.8 A, in nickel and iron chlorite respectively, corresponding to the 001 reflection are obtained. The intensities of these peaks considerably increase$ on heating the samples to 600°C but the 002, 003 and 004 reflections are drastically decreased in intensity on heating.

3. Characterization of these artificial chlorite samples, as observed from their Dehydration, Differential Thermal and Infra Red Spectrophotometric Analysis: (pp.48-49, 54-58, 64-73).

Further proof of the transformation of montmorillonite structure and the formation of chlorite structures is forthcoming from their dehydration and D.T.A. studies. The dehydration curves of these structures resemble with those given by Nutting for natural chlorites. In these curves, there is almost no loss of water before 200°C, showing the absence of adsorbed water. These curves also go to show that, like the naturally occuring chlorites, the OH water of these structures is lost in two stages.

The interesting features of the D.T.A. curves are: (i) the disappearance of the 700°C endothermic peak observed in the case of bentonite, (ii) the appearance of a sharp endothermic peak at 600°C in all these transformed structures, which is a characteristic of the chlorite mineral, (Mackenzie). Moreover, exothermic peaks, similar to those reported for the natural chlorite structures, in the temperature range 800° - 950°C are also observed.

Infra Red Spectra studies reveal that the bands, in the wave length region 800-1200 cm^{-1}, differ from bentonite and amongst themselves, in shape, number and intensity of the shoulder peaks. From these observations, it has been concluded that the silicate structure is destroyed to different extent, during the precipitation of the metal hydrous oxides between the unit sheets of montmorillonite. These results are in conformity with those of chemical analysis,(p. 53). Also, the position, intensity and number of minor peaks in the OH band stretching region varies from sample to sample, due to the difference in the bonding energy of OH for the metal present.

4. Cation exchange capacity of artificial chlorite structures: (pp. 42-47,51-52,61-64).

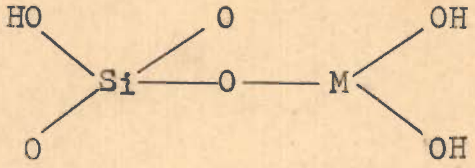
The large decrease in the c.e.c. values,(determined by analytical,flame photometric, and polarographic analysis), from 90 m.e.q. per 100 gm. of bentonite clay to about 12.0,16.0,25.0 and 32.0 m.e.q. per 100 gm. of nickel, magnesium,iron and aluminum chlorite respectively, confirms the transformation of bentonite to chlorite. The observed c.e.c. values for these various structures are in the range of 10-40 m.e.q. per 100 gm. clay,a range reported in the literature for the naturally occuring chlorites.

5. Electrometric titrations and the existence of Suspension effect in these structures:(pp.77-107, 148-169).

In the second chapter, the potentiometric and conductimetric titrations of these modified clay structures, both acid leached and ion-exchange by resin treatment,in aqueous and non-aqueous media, are discussed. The acid leached bentonite gives two inflexions in its electrometric curves, while only one inflexion is realized with the resin treated clay. The c.e.c.s, calculated from these curves, are almost the same in both the cases, (p. 100). Another interesting aspect of the studies is that the second inflexion of the acid leached bentonite disappears in the alcoholic medium. The "Levelling Effect" of the aqueous medium is clearly shown by the large difference in the pK values of these clay samples in the two media. The second inflexion point is supposed to occur due to the interaction of liberated aluminum ions with hydroxyl ions. These results are in conformity with the data of Lai, Mitra and Singhal and Malik.

Out of the four transformed chlorite like structures, the electrometric behaviour of aluminum chlorite is much different from that of iron, nickel and magnesium chlorite, due to the unique position of Al^{+3} ions,(by virtue of their size), in clay minerals. Besides, its hydroxide is amphoteric in nature, with the result that its colloid-chemical properties become very much pH-dependant. The first inflexion point in its titration curves may be due to the neutralization of H^+ ions,(alumino-silicic acid and other oxy salts of aluminum), present at low pH values, (pp.103-106).

The second inflexion point may be due to the dissociation of hydroxylic hydrogen from the acidic OH groups, of the metal, or from Si-OH linkages or both of the structures of the type



where M stands for metal ions.

The differences in the behaviour of these clay structures amongst themselves may be attributed to the difference in solubilities of the metal hydroxides.

Another interesting point emerging out of these studies is that the difference in c.e.c.s between the two inflexion points is 10 m.e.q. per 100 gm. clay, in the case of all these modified structures.

Electrometric titrations of the resin treated clays also reveal that the aluminum ions are not only liberated from the octahedral layers but with increasing acidity the displacement of these ions from the tetrahedral layers also takes place.

Electrometric titrations have provided a basis of differentiating between chlorites and other clay minerals. Chlorites give two inflexion points as compared to only one in the case of montmorillonites, but unlike kaolinites the ratio of c.e.c. at the two inflexions, is not equal to 2.0 in these structures. Also, in these structures the first inflexion point occurs in a much wider and acidic pH range, usually 4.0-8.0, than the pH range of 7.0-8.0 of kaolinite. These chlorites can also be differentiated from illites, attapulgites or nontronites as these latter structures give three inflexions in their electrometric titration curves.

Following the procedure adopted by Singhal and Malik, for the identification of clay minerals, with the help of Wiegner Pallmann Suspension Effect, interesting results were obtained with these modified clay structures. A distinction between bentonite and these artificial clays can be made from the plots of Δ pH (difference in pH between the supernatant liquid and the coagulated suspension) and sol concentration. In aqueous bentonite suspensions, acid range, there is a regular fall in Δ pH with increasing concentration of the sol, whereas in these chlorite structures a regular increase is observed. The fact that the pH of the suspension is always lower than the equilibrium liquid, suggests that when the dispersed micelles settle out, the H^+ ions are adsorbed on the floccules, (p.166).

An entirely different behaviour is observed in the alcoholic medium, where curves similar to those in the aqueous medium are obtained only on plotting $-\Delta$ pH against sol concentration. The fact that the adsorption of H^+ ions controls these changes is quite evident from these studies, (p.167).

Adsorption effects are not evident in suspensions studied in the alkaline medium. This would mean that OH^- ions are not adsorbed on the electrical double layers of the clay particles but remain free in the dispersion medium, (p.167).

The sol concentration effect studied in these clay minerals goes to show that the following equation of Loosjes is strictly followed:

$$(pH_{cs} - pH_{cs \to \infty}) (cs + K) = (pH_{cs = 0} - pH_{cs \to \infty}) K.$$

Although suspension effect can be profitably used to differentiate these chlorites from montmorillonite or kaolinite clays but it is not possible to differentiate the various chlorites(obtained from different metal hydrous oxides precipitation) amongst themselves,with the help of this suspension effect.

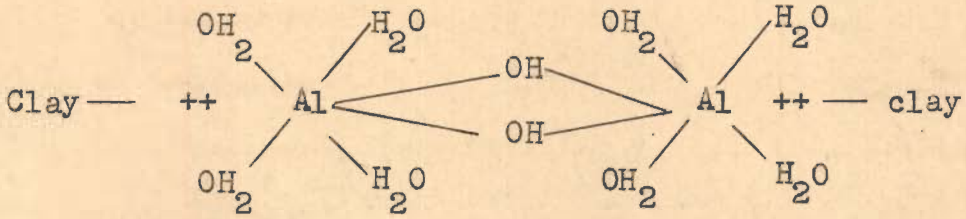
6. Viscosity variations with pH and the effect of the anions of the Hofmeister series:(pp.108-147).

Viscometric behaviour of these clay structures shows that the viscosity continuously increases with increasing concentration of the various alkalies added to suspensions, whose pH is 7.0. These observations suggest the absence of any peptizing effect of OH^- ions on the negative layers. Highest viscosity is observed with $Ca(OH)_2$,whereas NaOH gives the least viscosity. The results are in agreement with those of Gedroiz and Tuorila, (pp.141-142).

A study of the variations in viscosity with change in pH (in presence of fixed amount of electrolyte) reveals that both the anions of the Hofmeister series as well as pH of the solution influence these variations. The initial decrease in the pH-viscosity curves of bentonite has been explained due to the small amount of electrolyte present, which brings about a decrease in the layer charges. This resultsin a decrease in Edge to Edge association forces and a large increase in the Edge to Face repulsive forces, (p.142).

The initial decrease in pH-viscosity curves of magnesium chlorite is explained in a manner similar to that for bentonite, but the continuous increase after pH 7.0 can only be explained in terms of redistribution of charges in the two layers and subsequent Edge to Edge association. The continuous fall in viscosity in the case of ferric chlorite is attributed to the fact that the brucite type layer is without any charge,now,and these variations are simply due to the adsorption of the ions of the Hofmeister series on the clay particles. These differences can also be due to the difference in the solubilities of various hydroxides,as can be seen in the case of nickel and magnesium chlorite,(pp.142-144).

As in the case of electrometric titrations, the behaviour of aluminum chlorite is much different from the other three chlorites. Here not only the order of anions is changed but an initial increase,(instead of a decrease), in viscosity is observed. This may be due to the possible existence of unit like



in aluminum chlorite,(pp. 144 -146).

The order of the anions of the Hofmeister series for the variations in viscosity at pH 7.0 is citrate $>$ $SO_4 >$ acetate $>$ Cl $>$ $NO_3 >$ $ClO_3 >$ I $>$ CNS. This order exists for all the three chlorite structures viz., magnesium, iron and nickel chlorite, and is almost reverse of the order of anions for bentonite.

The viscometric data further suggests that the clay particles are of a hetrophilic nature i.e., the particles contain areas both of hydrophilic and hydrophobic character.

These studies, further, reveal that the original bentonite structure is completely changed, during this artificial transformation and that these transformed structures can be differentiated amongst themselves on the basis of their rheological behaviour. No such differentiation is possible on the basis of the viscosity data with their mixtures with $Ca(OH)_2$ or KOH or NaOH, as the behaviour towards these alkalies of all these structures is exactly the same.

7. Polarographic reduction at the dropping mercury electrode of the various clay suspensions: (pp.170-193).

The last chapter deals with the polarographic reduction of the various clay suspensions. This study has been initiated for the first time and a new approach for the identification of clay minerals, on the basis of their polarographic behaviour is presented.

Micka has shown that various insoluble substances, in the form of suspensions, undergo direct reduction at the d.m.e.. The most striking and important result of his investigations is that substances of similar chemical composition but of different crystallographic constitution behave differently, as regards their reduction at the d.m.e., (pp. 170-173).

Polarograms of the various clay sols, in their hydrogen form, are taken without the addition of any supporting electrolyte. The attention is focussed on currents other than the diffusion controlled ones. The effect of the addition of the various surfactants like gelatin, methyl red, cationic, anionic and non ionic soaps has been investigated, to elucidate the nature of such waves, (pp. 177-179).

The striking features of the reduction of the various clay minerals are, (i) the appearance of well defined polarographic reduction waves with $E_{1/2} = -1.6$ V, (ii) the existence of kinks or maximas in all the clay suspensions, except in the case of bentonite, at -0.3 V and (iii) the absence of any high migration currents even in the absence of a suitable supporting electrolyte, (pp. 180-184).

The polarographic wave with $E_{1/2} = -1.6$ V can be due to the reduction of hydrogen, but the fact that the height of this wave decreases on ageing indicates the existence of a mixed wave, due to the displacement of H^+ ions by Al^{+3} ions, (pp. 185-6). Distortion and subsequent disappearance of this wave on the addition of surfactants, except anionic soap, is found to take place. In the case of anionic soap the height of this original hydrogen wave increases since the soap, as such, is expected to give a hydrogen wave,

Inspite of the fact that the kinks or maximas appear at -0.3 V in all the clay minerals, except bentonite, their behaviour differs from clay to clay. Thus for chlorites and illites these kinks persist even on ageing, while for kaolinite these disappear under similar conditions, (pp. 186-189).

Addition of maxima suppressors throws more light on the nature of these kinks. The height of these kinks is either greatly suppressed or complete disappearance of these kinks takes place, on the addition of surfactants to kaolinite and illite sols, (for the latter even the emergence of a new wave in place of the kink is realized). The behaviour is altogether different with the artificially prepared chlorite like structures, where the addition of surfactants (except anionic soap) brings about an increase in the height of these kinks.

Based on various considerations, it has been shown that these kinks are not connected with the maximas obtained in the usual polarographic reduction waves. Their existence appears to be dependant on the physical state, (type of crystal lattice, size and shape of the colloidal micelles and surface area etc.), of the clay and not on the chemical constituents of which the clay is made of. From these polarographic studies, it has, further, been concluded that these kinks may be due to the adsorption of charged clay particles on the mercury drops. Effect of an outside resistance and surfactants on these kinks supports this view point, (pp. 188-189).

Reduction waves of metal hydrous oxide sols, used in the preparation of these chlorite structures, do not show any kink of the type described above. This is another significant observation, which goes to show that bentonite and metal hydrous oxides originally capillary inactive, become capillary active, when docked together, (pp. 189-191).

A table, for distinguishing the various clay minerals on the basis of their polarographic reduction data and the behaviour of the kinks obtained therein, has been drawn out, (p. 193).

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List of publications and symposiums attended.

1. On the constitution of metal hydroxide sols.

2. Electrometric titrations of bentonite in aqueous and non aqueous media.

   Both the papers presented at the 34th Annual Session of the National Academy of Sciences, India, held in Muzaffurpur, in Feb. 1965, and accepted for publication by the same.

3. Rheological properties of transformed montmorillonite structures (chlorites).

   Paper presented at the joint convention of Indian Chemical Society and C.S.I.R., held in Aligarh, in Dec. 1965 and communicated to J.I.C.S.

4. On the polarographic and flame photometric methods of measuring c.e.c. of natural and transformed clays.

   Paper presented at the 35th Annual Session of the National Academy of Sciences, held in Agra, in Feb. 1966, and communicated to J. Indian Soc. Soil Sci.

5. Polarographic behaviour of clay minerals.

   Communicated to Soil Science (America).

6. Electro-osmotic stabilization of soils with different metal anodes.

   Indian Society of Soil Science, J. (In Press).

7. Aggregate size distribution in wet and dry state by Yoder's water Stable analysis technique.

   Soil Science(America) 100, 319-322, 1965.

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