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The Interaction of Clay with Water and Organic Liquids as Measured by Specific Volume Changes and Its Relation to the Phenomena of Crumb Formation in Soils

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IX. *The Interaction of Clay with Water and Organic Liquids as Measured by Specific Volume Changes and its Relation to the Phenomena of Crumb Formation in Soils.*

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The densities of clay particles determined by the specific gravity bottle method vary somewhat according to the liquid used. Thus water, alcohol, and benzene all give slightly different values. The results show that some condensation of the liquid on the surface of the particles usually, if not invariably, takes place, indicating a certain amount of interaction between the clay and the liquid.

The investigation described in this paper shows that this interaction depends partly on the exchangeable bases associated with the clay, and partly on the molecular constitution of the liquid. The relations are as follows :

(1) No evidence could be obtained of interaction between clay and non-polar liquids.

(2) Interaction took place in all the polar liquids examined. Its amount was measured by the reduction in specific volume of the clay as compared with its volume in tetralin, a very convenient non-polar liquid for specific gravity determinations. This reduction in specific volume is approximately proportional to the number of exchangeable cations present, figs. 10, 11, and to the mean density of their surface charge, Table IV. Thus the order of effectiveness of the cations is : magnesium—most active, calcium, hydrogen, sodium, potassium—least active. This order is independent of the liquids used provided no chemical action takes place between the exchangeable cation and the liquid.

(3) A similar effect is produced by some other property of the clay associated with the shape of the titration curve.

(4) The amount of interaction depends on the liquid, but no simple relations with the molecular constitution have yet been discovered.

(5) During the process of removing the liquid by drying, the clay particles may aggregate to form definite crumbs.

The Phenomena of Crumb Formation

Considerable attention has been paid to crumb formation because of its importance in natural soils. Good tilth, which is essential for successful plant growth, is largely dependent on a stable crumb structure of the soil, and much of the art of cultivation consists in the production of this structure prior to the sowing of the seed. Considerable success has been attained by purely empirical methods, but hitherto no satisfactory explanation of the mechanism of crumb formation has been offered.

Crumb particles, similar to those found in nature, can be produced artificially in the laboratory by mixing clay with water and allowing it to dry under definite conditions. These crumbs are characterized by two distinct properties: they are hard when dry and they possess fairly characteristic shapes. The following are the main phenomena of crumb formation and stability brought out in the present investigations.

(1) Crumb formation is limited to those particles possessing considerable base exchange capacity. It is not shown by any of the kaolinitic clays of low base exchange capacity so far examined.

(2) Crumb formation is further limited to particles below a certain size. All the fine clay particles formed aggregates, though no fine clay has as yet been found with a low base exchange capacity. Silt particles of settling velocity exceeding $3 \cdot 5$ μ/sec. did not form aggregates however large their base exchange capacity might be.

The coarser clay minerals and the fractions devoid of base exchange are thus not essential for aggregate formation, but seem to serve only as a diluent, keeping the aggregates more open and mechanically weaker.

(3) Crumb formation is induced only by those liquids the molecules of which have an appreciable dipole moment. Thus water, methyl, ethyl, and amyl alcohols, and nitrobenzene, all gave definite aggregates, while benzene and carbonate tetrachloride gave no real aggregates at all.

(4) The hardness of the crumbs is dependent on the sizes of the clay particles, of the exchangeable cations and of the molecules of the wetting liquid. If any of these be large the aggregates formed are soft: only when they are all small are the aggregates hard. Thus, soft aggregates are formed from coarse clay particles, however large their base exchange capacity; from clays holding large complex cations such as phenyl-benzyl-dimethyl-ammonium; and from clays of small particle size and small cations wetted with liquids like nitrobenzene or amyl alcohol, although these same clays if wetted with methyl or ethyl alcohol form hard aggregates.

(5) The process of crumb formation may be reversible or irreversible; in the former process the crumbs fall down to a paste on rewetting, in the latter they do not, but remain stable. The stability depends on the liquid and on the exchangeable cations of the particles. Sodium clay aggregates are unstable in water, though stable in dry amyl alcohol. Calcium clay aggregates, on the other hand, are stable in water though unstable in dry amyl alcohol.

The formation of crumbs, therefore, appears to depend on an interaction between the exchangeable cations of the clay and the dispersion liquid.

The Mechanism of Crumb Formation

Clay particles suspended in water possess an electrokinetic potential and contribute, as SCHOFIELD* has shown, to the electrical conductivity of the suspension. This indicates that each particle is surrounded by an electrical double layer, the outer one being diffuse and consisting of cations, while the inner layer consists of negative charges presumably anchored on the surface of the particle. The cations in the diffuse layer move about in the water in the same way as they do around a complex anion, as pictured in the Debye-Hückel theory of strong electrolytes. Since the water molecules possess a dipole moment, they tend to be orientated along the lines of electric force radiating from each ion in the diffuse layer and from each free charge on the surface of the clay particle. Every cation and particle is thus surrounded by an envelope of orientated water molecules, and the orientation manifests itself as an apparent adsorption or immobilization of water by the clay. Some of the water molecules near an electric charge may be so strongly orientated that they appear bound to it, their heat motion merely making them oscillate about the lines of force, while those further away from the charge possess only a statistical orientation around it. A clay particle in a dilute suspension can, therefore, be pictured as consisting of a central core surrounded by a surface carrying a negative charge. Around each negative charge is an envelope of water molecules which are more strongly orientated the nearer they lie to the charge. Outside this surface are the cations, also possessing envelopes of orientated water molecules. Some cations are so close to a negative charge on the surface of the clay particle that the two water envelopes belonging to these charges overlap and the water molecules in this region are orientated in their joint field. This orientation is very strong, since the negative end of the water dipole is attracted to the cation and the positive end to the particle's surface, as shown diagrammatically in fig. 1.

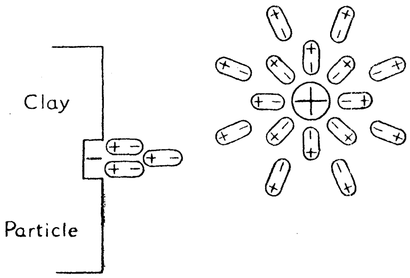

FIG. 1.

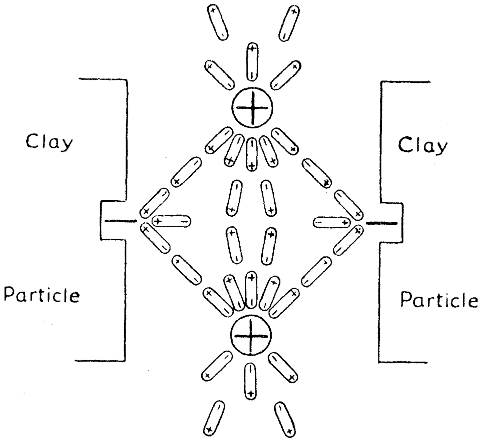

FIG. 2.

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* Unpublished data.

As the water is removed the deflocculated clay suspension becomes more concentrated and an increasing proportion of the water molecules become orientated in the joint field of a positive and a negative charge. It is reasonable to assume that a certain number of cations will share their orientated envelopes with two clay particles, as is shown diagrammatically in fig. 2.

A linking system is thus set up consisting of :—

particle—orientated wetting molecule—cation—orientated wetting molecule—particle.*

As removal of water proceeds, an increasing proportion of cations share their water envelopes with two clay particles, and so the number of links increases. The links also become stronger, because they become shorter and the mean orientating couple on the water molecules increases. In consequence, the cohesion of the clay particles, *i.e.*, the hardness of the crumbs, increases.

The hypothesis involves two assumptions, which have not yet been directly tested, though there is some indirect evidence in their favour :—

(1) that a system of the type postulated is in fact mechanically stable ;

(2) that the number of cations dissociating from a clay particle in a system that is losing water decreases less rapidly than the number of water molecules.

The hypothesis accounts for the formation of crumbs by other polar liquids as well as water, and for their non-formation by non-polar liquids. It also explains the necessity for the clays to possess dissociating cations, *i.e.*, base exchange capacity.

Further, it explains the observed relation between the hardness of the aggregates and the size of the clay particles, the cations and the molecules of the wetting liquid. For the smaller the clay particles, the larger the number of links per unit volume between them, provided the surface of the clay particle be curved and not plane. Again, a large univalent cation, such as the phenyl-benzyl-dimethyl-ammonium ion, has a much smaller surface charge density than a potassium ion, and so forms weaker dipole-cation-dipole links and therefore weaker aggregates than those of potassium clay. Finally, the strength of the bond between cation and clay particle increases with the dipole moment of the liquid, provided the position of the dipole in the molecule remains about constant. But if one end of the dipole becomes large, as for example in amyl alcohol and nitrobenzene where the positive ends are the groups C_5H_{11} or C_6H_5 while the negative end is the simple group -OH or -NO_2, then the positive end of these dipoles cannot be strongly attracted to the negative charges on the clay surface, and so cannot form a strong binding link. This is in agreement with the experimental result that hard crumbs can be formed from water and ethyl alcohol, when both ends of the dipole are small, but not from amyl alcohol or nitrobenzene.

Crumb formation is thus seen to occur when each end of the dipoles of the molecules of the wetting liquid is reactive, so that one end interacts with the negative charge on the clay particle and the other with the positive charge on the dissociated cation. If,

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* For convenience this is called in later paragraphs the dipole-cation-dipole link.

however, only one end of the dipole is strongly reactive, then hard crumbs are not formed though considerable interaction with the clay may still take place as shown by the reduction in specific volume. For example, clays interact as strongly with amyl alcohol as with ethyl alcohol, and with considerable diminution in specific volume in each alcohol, yet they form hard crumbs from ethyl and not from amyl alcohol.

The Influence of Electrolytes on Particle Cementation: Relation of Crumb Formation with Flocculation

The phenomena of crumb formation on drying after wetting with water are modified in the presence of electrolytes.

Two effects are produced :—

(1) the crumbs are smaller and weaker ;

(2) provided the concentration of the electrolyte exceeds a certain value all crumbs are stable in the solution of the electrolyte.

Both may be attributed to the reduction in dissociation of the cations from the clay surface caused by the electrolyte.

This reduces the number of dipole-cation-dipole links producible on drying and therefore weakens the resulting crumbs.

While crumb instability has not yet been studied in detail there is reason to connect it with the dissociation from the clay particles of a large number of cations having voluminous hydration or solvation envelopes. The presence of the electrolyte, by decreasing both dissociation and hydration of the cations, therefore increases the stability of the crumbs.

Analogies have often been traced between flocculation (*i.e.*, floc formation) in a clay suspension and crumb formation in a drying soil ; actually these analogies are not valid, the processes being different. Floc formation has recently been discussed by the author* for aqueous solution and by McDowell and Usher† for organic liquids. It occurs only when the electrokinetic potential of the clay particle is low, *i.e.*, when only small dissociation of the cations occurs. Crumb formation, on the other hand, occurs when there is an appreciable amount of dissociation of cations from the surface, *i.e.*, when the electrokinetic potential is high.

Flocs have a very open heterogeneous structure and a large volume in comparison with that of their component particles : they are weakly aggregated and can be broken up by shaking. Crumbs, on the other hand, have a much closer, more homogeneous structure, and can be much more strongly held together.

No satisfactory hypothesis has been put forward to account for the cohesion of clay particles into flocs and therefore no detailed comparison with the mechanism of crumb formation can be made.

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* 'J. Agric. Sci.,' vol. 22, p. 165 (1932).

† 'Proc. Roy. Soc.,' A, vol. 131, pp. 409, 564 (1931).

The essential difference between the two processes is brought out by comparing the effect of adding calcium chloride to a 5% suspension of calcium-clay in water, with the effect of adding sodium chloride to a 5% suspension of sodium-clay. The calcium-clay forms flocs which settle to a fairly loose sediment, but the sodium-clay forms no flocs while the whole suspension sets and becomes rigid and thixotropic. The calcium chloride strongly depresses the dissociation of calcium ions from the clay surface, so that floc formation can take place, while sodium chloride cannot depress the dissociation of sodium ions from the clay to anything like the same extent, so that floc formation cannot take place. The sodium and chloride ions introduced by the added salt, as well as the sodium ions that have dissociated from the clay, have envelopes of orientated water molecules around them, and so can form links of the type

$$\overset{+\quad -}{\text{(dipole)}}\ \overset{+}{\text{(cation)}}\ \overset{-\quad +}{\text{(dipole)}}\ \overset{-}{\text{(anion)}}\ \overset{+\quad -}{\text{(dipole)}}\ \overset{+}{\text{(cation)}}\ \overset{-\quad +}{\text{(dipole)}}$$

which can bind two clay particles together. This link is of the same type as the simple dipole-cation-dipole link illustrated in fig. 2, but it is longer, it can hold much more water and therefore becomes effective at much higher water concentrations. The length is responsible for the thixotropic behaviour of these rigid suspensions, since if the system is violently disturbed the binding links are broken down and take a certain time to build up again.

Experimental

Materials—Clays separated from the following soils were used in this investigation.

Alluvial or drift soils—Clay-with-flints (Rothamsted), Boulder clay (Samuelstown, Haddington), three London Clays (Whitstable, Herne Common and Chessington, near Surbiton), Carse soil (Larbert), Fen soil (Cambridgeshire), Gezira soil (Wad Medani, Sudan) and a Palestine soil (Mikveh-Israel).

Soils from solid formations—Old Red Sandstone (Putley, near Ledbury), Triassic Keuper Marl (Long Ashton), Lower Lias (Axminster), two lower Oolitic soils (Andoverford, Gloucester, and Redbourne Kirton-in-Lindsey) and an Oxford clay (Bampton Lew).

To prepare the separated clays, the soils were usually first treated with sodium hypobromite to oxidize and to bring into solution much of the organic matter, and to assist in the breaking up of the soil crumbs. The soil was then repeatedly dispersed in a large volume of dilute (0·05%) sodium carbonate. The material that remained in suspension in the top 20 cm after 24 hours' standing was then syphoned off and flocculated with dilute acid. The bases were then washed out, with dilute HCl (less than N/50) in the first series of separations, and with half-neutralized sodium acetate (p_H about 4·5) in the later series, until the supernatant liquid was calcium-free; the acid or sodium acetate was then washed out with distilled water until the clay was deflocculated. In the first series of experiments the clay was divided into aliquots, and each was saturated with a given base by adding the corresponding acetate. The acetates were added repeatedly until the p_H of the supernatant liquid was about 7, when the alkaline-earth acetates were washed out with distilled water, and the alkali acetates with distilled water followed by alcohol. In the second series of experiments the purified hydrogen or sodium clay was passed through a Sharples supercentrifuge to remove the coarse clay and fine silt particles present, so that the deflocculated clay suspension would not settle appreciably during preparation, thus ensuring that the crumbs produced should have as uniform composition as possible. Instead of preparing the different homionic clays—that is, clays containing only one exchangeable base—by adding the acetate, either of two buffer solutions were used: half-neutralized *p*.nitrophenol—p_H about 7, and half-neutralized acetate—p_H about 4·5, in each of which the base concentration was N/50.*

The liquids used for wetting were, whenever possible, of A.R. standard of purity, and were always dried either over phosphorus pentoxide or over freshly ignited lime for 3–4 weeks and distilled just before use. No more refined drying technique was employed, as the liquids were in contact with the air for short periods and so could absorb traces of water vapour just before and just after wetting the crumbs.

The Experiments on Crumb Formation and Crumb Stability

(*a*) *Relation of particle size to hardness of aggregates*—Silt fractions were separated from the Carse, Lower Lias and Gloucester soils, and coarse clay fractions from the Gloucester and one of the London clay soils. The coarser materials were easily separated from the silt and clay by sedimentation, the silt used having a settling velocity between 20 and 3·5 μ/sec. The fine clay crumbs were dispersed by repeated alternate treatment with sodium hypobromite and boiling with hydrogen peroxide, and the clay was removed by repeated dispersion in sodium carbonate. These treatments were continued until no appreciable amount of clay came into suspension. The coarse clay fractions were prepared from the complete clay fraction by passing the deflocculated clay through a Sharples supercentrifuge, removing the coarse fraction from the bottom of the bowl and repeatedly passing this fraction through the centrifuge to remove the finer clay particles from it. The settling velocities of these clay particles cannot be calculated from their method of preparation, nor has an ultra-microscopic count been made on the dispersion, so that it is only possible to give the upper limit of their settling velocities, namely, 3·5 μ/sec. The base holding power of these materials between SCHOFIELD'S† hydrochloric acid level and his *p*-nitrophenol level are in milli-equivalents/100 grams :—

For the silts : Carse 2·2, Lower Lias 3·5, Gloucester 10·8 ;
For the coarse clays : Gloucester 33·5, London I 23·2.

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* The author is indebted to Dr. R. K. SCHOFIELD for bringing to his notice the advantage of using strongly buffered solutions for the preparation of homionic clays, and for suggesting the most appropriate weak acids to use.

† 'J. Agric. Sci.,' vol. 23, p. 252 (1933).

On drying, or on freezing and drying from a water dispersion, these materials formed weak blocks. The silts broke down immediately to a fine powder when touched with the finger, while the coarse clays had to be rubbed between the fingers.

(*b*) *Relation of size of the exchangeable ion to hardness of crumb.*—Two separate fractions of a Gloucester clay, a medium fine and a very fine fraction, were divided into five aliquots, which were saturated up to p_H 7 with Ca, Na, K, Mg and phenyl-benzyl-dimethyl-ammonium. The phenyl-benzyl-dimethyl-ammonium chloride was prepared by adding equimolecular quantities of dimethyl aniline and benzyl chloride in absolute alcohol, leaving in the dark for one month and precipitating the salt with ether. The crystals were then washed with ether, redissolved in alcohol, reprecipitated and rewashed with ether and dried. The acetate or chloride was then washed out, and the deflocculated clay paste either frozen or, if it was the sodium or potassium clay, dried. For each of the calcium and magnesium clays hard crumbs, diameter about 3 mm, were formed when dry, but for the substituted ammonium clay the crumbs were smaller and crumbled between the fingers to a fine powder; this clay held nearly 60 milli-equivalents of exchangeable base per 100 grams, and fully deflocculates only with difficulty. When dry it has a very faint smell of dimethyl aniline.

(*c*) *Relation of wetting liquid to hardness of crumbs*—Clay dispersions made up in different liquids were obtained from the deflocculated clay in water by removing the water with alcohol, the alcohol with the required liquid or with benzene, or the benzene with the required liquid. At each renewal of the liquid the clay was shaken for several hours to ensure good dispersion. The liquid was removed with Berkefeld filter candles attached to a water pump through sulphuric acid bottles, only dry air being admitted to the bottles containing the clay. Freshly distilled dry liquids were always used finally. These clay dispersions were then dried at 80° C over P_2O_5 in a desiccator kept at a low pressure with an oil pump containing an ice condenser and silica-gel adsorption tubes in the vacuum circuit. Hydrogen-clays separated from the Old Red Sandstone, Lower Lias and London Clay soils, and a calcium London clay gave only extremely soft aggregates from benzene and carbon tetrachloride, not quite so soft from amyl alcohol, and hard from ethyl alcohol dispersions, while definite, though fairly soft, crumbs were formed by freezing and drying a nitrobenzene dispersion of the hydrogen Lower Lias clay.

(*d*) *Relation of wetting liquid to stability of crumbs*—If a crumb formed by freezing a water paste of a calcium clay is thoroughly dried and then wetted with dry amyl alcohol under vacuum it usually, though not always, broke down into a paste, but no sodium clay crumb broke down. It was also found that a deflocculated suspension of a calcium clay can readily be formed in dry amyl alcohol, while it has not yet been possible to deflocculate a sodium clay in it.

Determination of the Specific Volume of the Clays

To determine the specific volume of the clays, about 10 grams of clay crumbs were put in a 25-cc specific gravity bottle, placed over P_2O_5 in a desiccator, which was evacuated by the oil pump, and left for a week. Fresh P_2O_5 was then put in, the desiccator re-evacuated and left for at least two weeks, and this stage would be repeated unless the surface of the P_2O_5 was still powdery. For non-volatile liquids wetting was carried out under vacuum with the oil pump running, but for volatile liquids, such as water or the alcohols, this method was not satisfactory, since the clay crumbs would be shot out of the bottle as the liquid came into contact with them. For volatile liquids two different methods of wetting were used. In the first, after the crumbs had been evacuated for about 20 minutes, the vacuum circuit was shut and the liquid was run into the bottom of the desiccator, and after this had been left for about 10 minutes fresh liquid was then run into the bottles containing the crumbs. This method was still not very satisfactory as some bumping often occurred when the liquid first came in contact with the clay. In the second method tried, the desiccator was evacuated, then a stream of the vapour was passed over the crumbs to enable them to adsorb an appreciable amount of the liquid, then the liquid itself was run into the bottles. This method, which was used only at the end of the experiments, was much more satisfactory. After the clay had been wetted under vacuum, the bottles were put into closed tanks containing dry paraffin for 3–6 hours, these tanks being immersed in a large water thermostat tank running at about 25° C. Three hours was found to be sufficiently long to allow the clay to reach equilibrium with the liquid.

In the calculation of the apparent specific volume of the clay crumbs the density of water was always assumed to be that given in LANDOLT-BÖRNSTEIN'S tables, all other densities being calculated from this. Buoyancy corrections were applied to the weights of the clay and of the liquids, the air density being determined each time from the barometer, thermometer and wet and dry bulb readings with the use of LANDOLT-BÖRNSTEIN'S tables. The differential buoyancy correction needed for the layer of adsorbed liquid was not large enough to be significant. The error introduced in the determination of the specific volume of the clays under the experimental conditions, due to limitations in the accuracy of the instruments used, is about 10^{-4}, this being caused by errors of $0 \cdot 1$ mg in the weighings and $0 \cdot 05°$ C in reading the temperature in the thermostat, these two sources of error being about equal. The only large sources of error are loss of clay from the bottles during wetting under vacuum, entrapping of air, and loss of liquid by evaporation between taking the bottle out of the thermostat and weighing it. Each of these three sources of error will make the specific volume of the clay appear too large, and as a matter of fact no case has yet arisen where the specific volume appeared to be obviously too low. Duplicate determinations were not made together, and everything possible was done to make the maximum amount of systematic error occur as random error between duplicates. From a study of the actual deviations between 400 duplicate determinations of the specific volume of the clays available, only 43% had divergences less than $2 \cdot 5 \times 10^{-4}$, in 25% it was between $2 \cdot 5$–$5 \cdot 0 \times 10^{-4}$, in 12% between 5–10×10^{-4}, and in 20% it exceeded 10^{-3}. Thus in 20% of the duplicate determinations at least one of the determinations had an error of 10^{-3}, so that at least 10% of the individual determinations had to be rejected owing to one of the three major sources of error, of which loss of clay during wetting under vacuum was the most common. It thus appears probable that the error of the mean is usually about $2 \cdot 5 \times 10^{-4}$. It is possible to make an independent estimate of this error, for some of the determinations were repeated at different times, and by comparing the differences between their means, approximately the same figure is obtained. In conclusion, therefore, the error in a difference between means will be about 5×10^{-4}.

Specific Volume of Clays in Different Liquids

Few of the methods devised in general colloid science to measure the interaction of a liquid or gas with a solid substrate have been, or can be, applied to clays, and so far no systematic investigation of this interaction in clays has been undertaken. The method adopted by the author has been to measure the apparent density of carefully dried soil and clay crumbs in different liquids. This method, which was first used by WILLIAMS* and CUDE and HULETT† for charcoal, seems to have been used for soils only by ANDERSON and MATTSON,‡ who found that dried separated clays appeared to be heavier in water than in toluene, and by TSCHAPEK§ who found that soils appeared heavier in water than in the four hydrocarbons benzene, xylene, petrol, and petroleum (? paraffin), in which the density was about the same. The method has the disadvantage that the results are not easy to interpret, since four separate factors can influence them :—

(1) the interaction of the particle surface with the dispersion medium ;

(2) the proportion of the total surface area of the clay particles forming the crumbs accessible to the wetting liquid ;

(3) the compression of the liquid in the fine capillaries of the crumbs due to the large curvature of the solid-liquid interfaces ;

(4) the amount of adsorbed and entrapped gases in the crumbs after wetting.

The adsorbed and entrapped gases are usually removed by a strong outgassing by keeping the system at a high temperature and a very high vacuum for a considerable time, but this method is probably inapplicable to clays as certain irreversible processes seem to attend high temperature dehydration, 100-200° C, though this point has never been adequately examined. For this reason, and also because the work was largely explorative, no elaborate degassing technique was employed, wetting being carried out slowly in a desiccator connected to a small rotary Hyvac oil pump.

The experiments were designed to show the influence of the exchangeable ions, held by a clay, on the apparent specific volume of the clay when immersed in different

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* 'Proc. Roy. Soc.,' A., vol. 98, p. 223 (1920).

† 'J. Amer. Chem. Soc.,' vol. 42, 391 (1920).

‡ 'U.S. Dept. of Agric. Bull.,' 1452 (1926).

§ 'Kolloidzschr.,' vol. 63, p. 34 (1933).

liquids. Separated clays were used, as very uniform crumbs can be obtained from them, so that sampling errors are negligible compared with other sources of error. This condition can barely be obtained with soils, for during the preparation of a soil holding one metallic cation only, the coarse and fine fractions become partially separated, through the crumbs breaking down in the solutions used, and it is very difficult thoroughly to remix all the materials. Since it was also considered more important to use only a few liquids but as many clays as possible, only two liquids, water and tetralin (tetrahydronaphthalene), were used for every clay, though amyl alcohol, aniline and nitrobenzene were also used for most of them. Isolated experiments in a number of other liquids were also made. Considering these five liquids only, the specific volume of a clay was greatest in tetralin and next in nitrobenzene without exception. With the exception of some of the hydrogen clays, the specific volume in aniline was greater than in water, and greater in amyl alcohol than in water, with the exception of the magnesium and one of the calcium clays, and about the same in amyl alcohol and aniline for the sodium, potassium and most of the calcium clays. Since the specific volume of a clay is greatest in tetralin, these data will first be examined to see how far they support the hypothesis that tetralin has no interaction with the exchangeable ions on the clay.

The specific volumes of clays in tetralin—The specific volume of a clay in a liquid depends on the following factors :—

(*a*) the specific volume of the clay substrate ;

(*b*) the weights and volumes of the exchangeable ions on the clay ;

(*c*) the interaction between the exchangeable ions on the clay particles and the wetting liquid ;

(*d*) the interaction between the clay substrate and the wetting liquid ;

(*e*) for dried clay crumbs the sizes of the pores in the clay crumb, these determining both the accessibility of the liquid molecules to the clay surface, and the compression of the liquid in the pores due to interfacial tension forces.

By considering the apparent specific volumes of different ionic clays in a given liquid, it should be possible to decide if the variations between the specific volumes of a clay holding different exchangeable ions can be accounted for completely by the weights and volumes of the exchangeable ions; if so, the exchangeable ions would have no differential effect on the total volume of the fine pores in the crumbs, nor any differential interaction with the wetting liquid.

The contribution of the exchangeable ions to the specific volume of the clay can be calculated as follows. Let σ_x and σ_y be the specific volumes of a clay holding B equivalents of ion X and ion Y respectively in a given wetting liquid, and let V, V_x and V_y be the volumes of one equivalent of clay, ion X and ion Y respectively and M_x and M_y the equivalent weights of the two ions, then

$$\sigma_x = \frac{V + BV_x}{1 + BM_x}, \text{ and } \sigma_y = \frac{V + BV_y}{1 + BM_y}$$

or, on eliminating V

$$\sigma_y = \sigma_x \left(\frac{1+\mathrm{BM}_x}{1+\mathrm{BM}_y}\right) - \mathrm{B}\left(\frac{\mathrm{V}_x - \mathrm{V}_y}{1+\mathrm{BM}_y}\right).$$

The two denominators of this equation can be expanded, and all except the first two terms of each expansion ignored since BM_y does not exceed 0·03 in any of the clays considered, giving as an approximate equation

$$\sigma_y - \sigma_x = \mathrm{B}\sigma_x(\mathrm{M}_x - \mathrm{M}_y) - \mathrm{B}\,(\mathrm{V}_x - \mathrm{V}_y). \quad \dots\dots\dots (1)$$

Unfortunately, although M_x and M_y, the equivalent weights, are known, V_x and V_y, their equivalent volumes, are not, so that this equation cannot be used to calculate $\sigma_y - \sigma_x$. Using the experimentally determined values of σ_x and σ_y for a series of clays, it is, however, possible to examine whether $\mathrm{V}_x - \mathrm{V}_y$, calculated from this equation, is independent of the type of clay used, and so dependent solely on the ions X and Y, and whether the observed values of $\mathrm{V}_x - \mathrm{V}_y$ appear reasonable on other grounds. The results given in table I, show that $\mathrm{V}_x - \mathrm{V}_y$ is nearly independent of the clay type, though, owing to the large experimental errors attached to this difference, it is not possible to say if the values for individual clays really differ significantly. Table I also shows that, per equivalent, the ionic volume of the ions increase in the order sodium, hydrogen, calcium and potassium, magnesium.

It is possible to obtain further evidence for the validity of these results from an analysis of the differences in molecular volume between different crystals belonging to the same system. For example, the densities of sodium chloride and potassium chloride crystals are given in the International Critical Tables as 2·163 and 1·988, and both belong to the cubic system. Hence, one mole of sodium chloride occupies 27·0 ccm and of potassium chloride 37·5 ccm, so that one mole equivalent of potassium is 10·5 ccm larger than one equivalent of sodium, on the assumption that the whole difference in volume between the sodium and potassium crystals is taken up by the larger size of the potassium ion, and ignoring all volume changes due to differences of packing. This calculation can be made for a large number of similar sodium and potassium crystals, and for the six available monovalent anions tabulated in the International Critical Tables the value of $\mathrm{V}_{\mathrm{K}} - \mathrm{V}_{\mathrm{Na}}$ varies from 12·6 to 10·3, with a mean of 11·3 ccm, though for the divalent anion crystals the figure is rather lower. This is very close to the value 11·1 ccm determined from the specific volume of the clays. The difference between the calcium and magnesium ions is more difficult to determine since the crystals of the corresponding salts usually belong to different systems, though it seems to vary from about 6—11 ccm with a mean of about 8 ccm per mole, so that $\mathrm{V}_{\mathrm{Ca}} - \mathrm{V}_{\mathrm{Mg}} = 4$, and from the scanty data available $\mathrm{V}_{\mathrm{Na}} - \mathrm{V}_{\mathrm{Ca}}$ is about 3 ccm. Since the results from the density calculation are $\mathrm{V}_{\mathrm{Mg}} - \mathrm{V}_{\mathrm{Ca}} = 14·6$ and $\mathrm{V}_{\mathrm{Ca}} - \mathrm{V}_{\mathrm{Na}} = 10·0$, these two sets of results are neither in quantitative nor qualitative agreement. Thus, while the difference between the volumes of sodium and potassium ions on a

TABLE I—Calculated Difference in Specific Volumes of Different Ions on Clays

	Bases held milli-equiv/ 100 grams	Ca — Na.			H — Na.		K — Na.		Mg — Ca.		
		$\Delta\sigma$ (obs.) $\times 10^{-5}$	$V_{Ca} - V_{Na}$ cc/equiv	$\lambda_{Ca} - \lambda_{Na}$‡	$\Delta\sigma$ (obs.) $\times 10^{-5}$	$V_H - V_{Na}$	$\Delta\sigma$ (obs.) $\times 10^{-5}$	$V_K - V_{Na}$ cc/equiv	$\Delta\sigma$ (obs.) $\times 10^{-5}$	$V_{Mg} - V_{Ca}$ cc/equiv	$\lambda_{Mg} - \lambda_{Ca}$‡
Trias	20·2	125 (10)*	5·1	0·92	250 (13)	4·5	77 (32)	9·5	312 (6)	12·7	1·80
Rothamsted	22·7	303 (45)	12·2	1·74	422 (46)	10·5	169 (45)	13·3			
London I	38·2	688 (51)	16·9	2·25	664 (43)	9·3	275 (55)	13·1	589 (61)	12·6	1·84
London III (*a*) ...	33·3	249 (56)	6·4	1·04	521 (30)	7·5	184 (63)	11·4	728 (27)	19·1	2·60
(*n*) ...	38·6	472 (125)	11·2	1·63	644 (16)	8·5	231 (39)	11·9	660 (130)	16·5	2·30
Lower Lias, Ser. I ...	40·7	316 (17)	6·6	1·15	640 (32)	7·2	161 (37)	10·1	479 (64)	8·3	1·43
Ser. II (*a*)	31·1	321 (54)	9·2	1·46	635 (47)	11·8	81 (4)	8·8	460 (53)	18·2	2·60
Carse, Ser. I	42·8	555 (46)	11·8	1·78	840 (75)	10·9	208 (56)	11·1			
Ser. II (*a*) ...	33·0	371 (47)	10·0	1·60	552 (112)	7·8					
Kirton-in-Lindsey (*a*)	54·5	473 (77)	8·9	1·42	918 (128)	8·1					
(*n*)	62·7	736 (100+)	11·2	1·68	1,290 (84+)	11·9					
Gloucester (*a*) ...	40·8	417 (55)	9·0	1·46	265 (71)	— 2·2					
(*n*) ...	58·8	603 (88)	9·1	1·46	522 (74)	0·1					
Gezira	65·0	859 (34)	12·1	1·73	1,477 (11)	14·3					
Mean	—	—	10·0	1·52	—	10·2†	—	11·1	—	14·6	2·11

* The figures in brackets give the variation from the mean obtained by taking the extreme values of each determination. For example, the individual determinations of the specific volume of the calcium and sodium Trias clays in tetralin are

Ca 0·35556, 0·35548, Na 0·35421, 0·35433

giving as the extreme values for Ca–Na 0·00135 and 0·00115. Since the mean value of the difference is 0·00125, this gives, in the above notation, a difference of 125, with an extreme variation of ± 10 from this mean.

† The figures for the Gloucester clays omitted.

‡ Assuming $V_W = 15\cdot5$ cm.

clay is, on the above assumptions, about the same as their difference in crystals, this does not hold for the sodium-calcium or magnesium-calcium differences.

A possible explanation of this discrepancy is the neglect of the water molecules attached to the exchangeable ions on the clay, for it has so far been implicitly assumed in the calculations that the exchangeable ions on the dried clays used were either themselves dry or all contained the same number of molecules of water of hydration, an assumption that is almost certainly false. The effect of these water molecules on the specific volume of the different ionic clays can easily be evaluated. Let each type of ion X have λ_x molecules of water attached to each equivalent of X, and let V_W be the mean volume occupied by 1 mole of water of hydration, and further assume that V_W is independent of the exchangeable ion, then using the same notation as before, the specific volumes of a clay holding B equivalents of ions X and Y respectively are

$$\sigma_x = \frac{V + B(V_x + \lambda_x V_W)}{1 + B\,(M_x + 18\lambda_x)} \quad \text{and} \quad \sigma_y = \frac{V + B(V_y + \lambda_y V_W)}{1 + B\,(M_y + 18\lambda_y)}$$

giving as the equivalent of equation (1)

$$(\sigma_y - \sigma_x)/B + \sigma_x\,(M_y - M_x) = (V_y - V_x) + (\lambda_y - \lambda_x)\,(V_W - 18\sigma_x). \quad . \quad . \quad . \quad (2)$$

Now the quantity on the left-hand side of this equation has been tabulated in Table I under the heading $(V_y - V_x)$. If now this quantity is written as ΔV (obs) and the true value of $(V_y - V_x)$ is written as ΔV (true), then

$$\lambda_y - \lambda_x + \frac{\Delta V\,(\text{obs}) - \Delta V\,(\text{true})}{V_W + 18\sigma_x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If it is assumed that ΔV (true) is the value of $(V_y - V_x)$ calculated from crystal density data, and if V_W, the volume of 1 mole of water of hydration, is assumed to have the same value as 1 mole of water of crystallization has in a crystal, then $\lambda_y - \lambda_x$, the difference in hydration between one equivalent of Y and of X can be calculated from this equation. Unfortunately V_W is not easy to determine, as the addition of water of crystallization to a crystal usually alters the system to which it belongs. Ignoring this alteration of system, it seems to vary from 13-18 in most substances examined, though usually it lay between 14-16 ccm with an average of about 15·5 ccm. The values of $\lambda_{Ca} - \lambda_{Na}$ and of $\lambda_{Mg} - \lambda_{Ca}$ have been calculated for all the clays available by using the crystal values $-$ 3·3 ccm and $-$ 4·0 ccm for ΔV (true) and by using $V_W = 15{\cdot}5$ ccm, and are given in Table I. As is seen from this table, the mean values of $\lambda_{Ca} - \lambda_{Na}$ and of $\lambda_{Mg} - \lambda_{Ca}$ are 1·52 and 2·11 respectively. Thus, one equivalent of calcium has, on the average, 1·5 more moles of water than one equivalent of sodium, so that 3 more molecules of water of hydration are attached to each calcium ion than to each sodium ion. Similarly, each magnesium ion has about 4 more molecules of water of hydration than each calcium ion. As a consequence of the assumption that the specific volume of a clay measured in tetralin is its true specific volume, then on a carefully dried clay the sodium and potassium ions have the same number of molecules of water of hydration, the calcium ion has about 3 more, and the magnesium ion $3 + 4 = 7$ more molecules.

An attempt was made to obtain independent evidence for the correctness of this conclusion by igniting the dry Trias and London I clays in an electric furnace at 650° C for 2 hours, in the hope that at this temperature the ions would have lost all their water of hydration, though unfortunately, owing to lack of time, the clay samples could only be dried at 110° C for 20 hours instead of being much more intensively dried over fresh P_2O_5 for several weeks in a vacuum desiccator. The results for the two clays were consistent, and showed that the magnesium ion has 3·5 more molecules of water of hydration than the potassium ion, the calcium ion 2·2 more, and the sodium only 0·5 more. Quantitative agreement between the results of this method and those derived from the specific volume of the clays in tetralin would not be expected, but both methods show that the exchangeable ions on an intensively dried clay can hold water of hydration.

The specific volume of clays in other non-polar liquids—Only a few experiments have been made on the apparent specific volume of clays in other non-polar liquids besides tetralin, but the results indicate a sharp difference in behaviour between soil and clay crumbs. Tschapek (*loc. cit.*) using two soils and four non-polar liquids, and the author using only one soil (Rothamsted) and six liquids non-polar or of very slight polarity (benzene, toluene, xylene, paraffin, tetralin and decalin) found that the specific volume of the soil was the same in all the hydrocarbons used within the limits of experimental error. For the few clays examined, which include a Rothamsted separated clay, the apparent specific volumes of dried clay crumbs are different in different hydrocarbons, being largest in decalin and carbon tetrachloride, next in tetralin and paraffin, then in xylene, and smallest in benzene. These differences, though definite, are not large, as all these specific volumes are larger than the specific volume of the dry crumbs in nitrobenzene, which gives the largest specific volume of the polar liquids used. The simplest explanation of this result is that the exchangeable ions do not interact with the hydrocarbons, but that appreciable capillary condensation of the liquid occurs in the pores of the dry clay crumbs though not in the pores of the dry soil crumbs. This explanation needs the assumption that the pores in a soil crumb are larger than in a clay crumb, an assumption that is almost certainly true, although not enough is known about the actual pore size in the crumbs to judge if this is sufficient to cause the difference.

Specific volume of clays in polar liquids—This discussion will be limited to the differences between the specific volumes of a clay in water, amyl alcohol, aniline or nitrobenzene and in tetralin. Let T and $L_{1\ 2\ 3\ \text{or}\ 4}$ be the specific volumes of a clay in tetralin and in one of the four liquids just mentioned, then $(T - L)$ will give a quantity from which the density of the clay substrate and equivalent weights and volumes of the exchangeable ions have been eliminated, and which is therefore controlled by differential capillary condensation effects and by the differential interaction between the clay and the two liquids. These quantities (T — L) have the following properties :—

(1) for a given exchangeable ion on the clay (T — L_1) is proportional to (T — L_2) for different clays. Fig. 3 shows that for hydrogen clays (T — N) is approximately proportional to (T — W), where T, N, W are the specific volumes of the clay in tetralin, nitrobenzene, and water respectively; and fig. 4 shows that for both hydrogen and calcium clays (T — Am) is approximately proportional to (T — W) where Am is the specific volume of the clay in amyl alcohol;

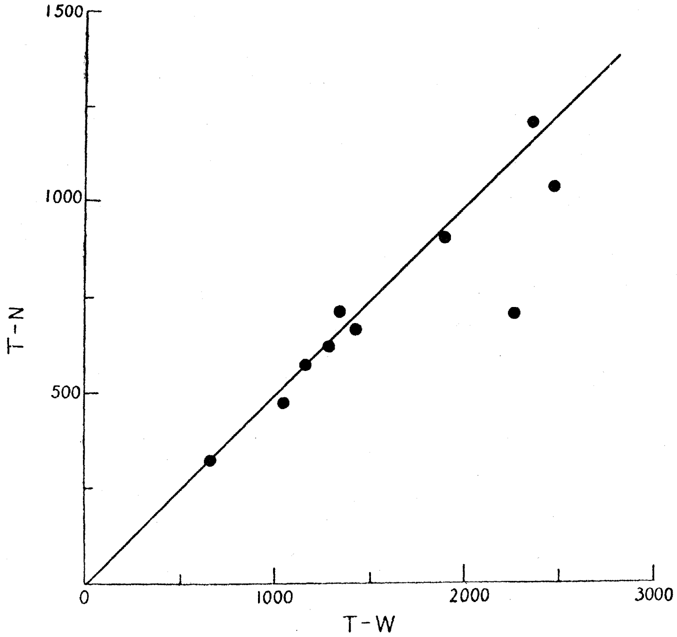

FIG. 3.—Specific volume reduction of hydrogen clays in nitrobenzene compared to water.

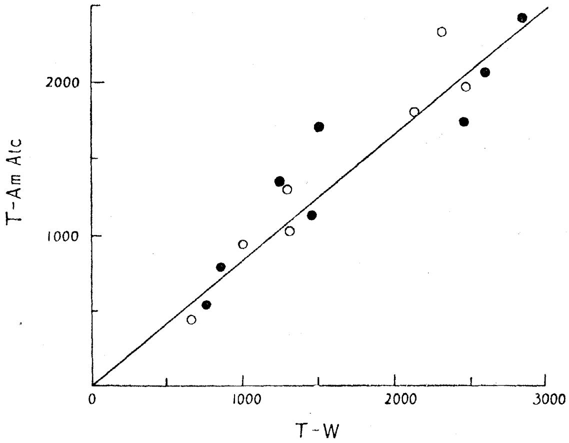

FIG. 4.—Specific volume reduction of hydrogen and calcium clays in amyl alcohol compared to water. ○ hydrogen clays; ● calcium clays.

(2) for a given liquid and a series of clays (T — L) for one exchangeable ion is proportional to (T — L) for a second. This is illustrated in figs. 5 and 6, in which (T — W) for the calcium clays is plotted against (T — W) for the corresponding sodium, potassium, magnesium and hydrogen clays, and in figs. 7, 8, 9, in which (T — L) for the calcium clay is plotted against (T — L) for the corresponding hydrogen clays where L is nitrobenzene, aniline, or amyl alcohol. These two generalizations, though only approximately true, suggest that this quantity (T — L) is largely controlled by the exchangeable ions on the clay, and not by the clay substrate itself.

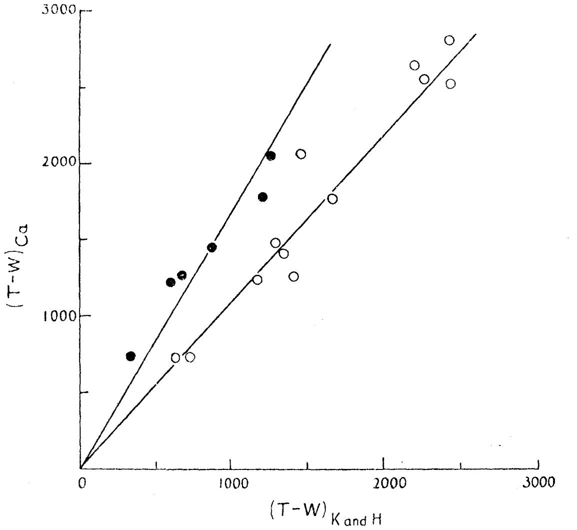

FIG. 5.—Specific volume reduction of potassium and hydrogen clays in water compared to calcium clays. ● Potassium clays ; ○ hydrogen clays.

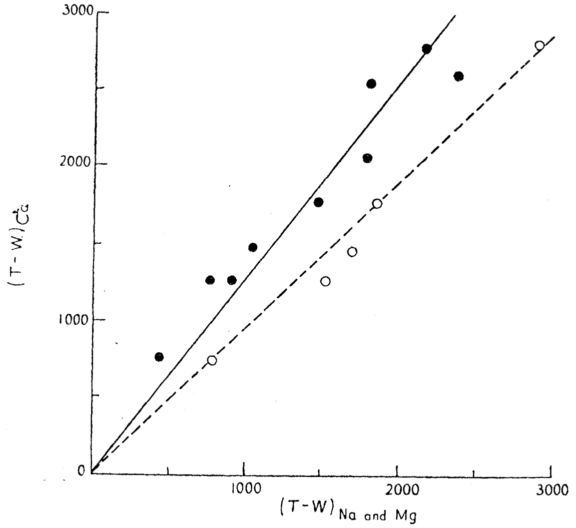

FIG. 6.—Specific volume reduction of sodium and magnesium clays in water compared to calcium clays. ● Sodium clays ; ○ magnesium clays.

(3) (T — L) depends on the base holding power of the clay, since (T — W) for the hydrogen clay is nearly proportional to its base holding power at p_H 7, fig. 10, and since (T — W) for those calcium clays which are nearly saturated up to p_H 7 with calcium is nearly proportional to the calcium held by the clay, fig. 11. Thus (T — L) is approximately proportional to the exchangeable ions held up to p_H 7. The ratio of these two quantities, which gives the mean reduction of specific volume of the clay in water from that in tetralin per equivalent of exchangeable ion, will be called the mean interaction value of that ion.

To investigate what proportion of the total hydrogen ions, that can be exchanged from a clay, take part in this interaction, the relative constancies of the different ratios (T — W)/B (x) for all the hydrogen clays available have been compared, where B (x) is the equivalents of calcium one gram of hydrogen clay can take up from a calcium buffer solution of p_H (x) and N/50 in calcium. The following variates were used for B (x) :—*

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* For a description of the experimental methods used to measure the various B (x), see SCHOFIELD, R. K., 'J. Agric. Sci.,' vol. 23, 252 (1933) and 'Trans. VIth Comm. Int. Soc. Soil Sci.,' B, p. 80 (1933).

B (HCl — Ac), B (HCl — N) and B (HCl — P). These variates denote the additional equivalents of calcium held per gram of clay in a solution of half-neutralized calcium acetate (p_H 4·5), half-neutralized calcium *p*-nitrophenol (p_H 7), or half-neutralized calcium phenol (p_H 9·8), respectively, in excess of the bases held by the clay in a solution of 0·04 N HCl and 0·01 N metallic chloride ;

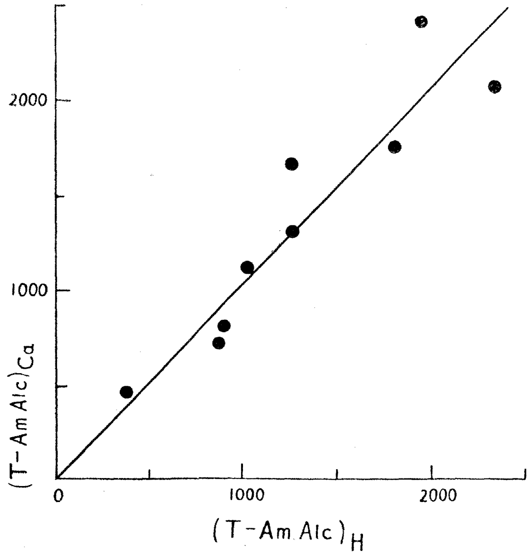

Fig. 7—Amyl alcohol

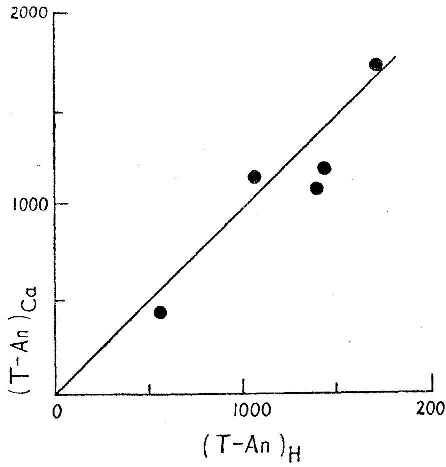

Fig. 8—Aniline

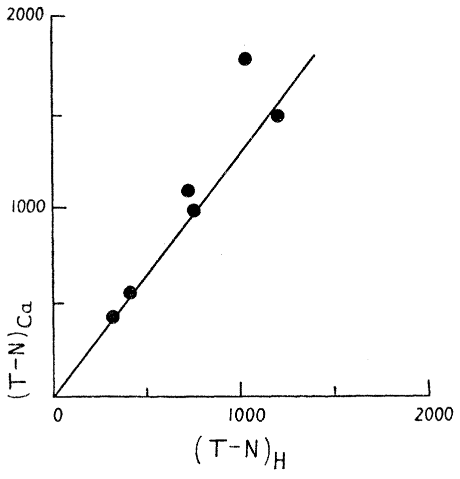

Fig. 9—Nitrobenzene

Figs. 7, 8, 9.—Specific volume reduction of hydrogen clays in different liquids compared to calcium clays.

B (Chl Ac — N), denotes the corresponding additional quantity of calcium held in the nitrophenol solution in excess of the calcium held in a half-neutralized solution of calcium chloracetate (p_H 2·8) ;

B (N), B (P), denote the equivalents of calcium taken up per gram of clay from the

p-nitrophenol and the phenol buffers respectively. For every hydrogen clay used these two fall between the hydrochloric acid and the chloracetate values.

In Table II are given the individual values of (T − W)/B (x) for all the hydrogen clays available, and the relative constancy of these ratios can be compared by computing the percentage deviation 100 S/M of the individual clays from their mean M for each ratio, where S is the standard deviation of the individual (T − W)/B (x) values for the clays from their mean M. The smallest percentage deviation is shown by using B (Cl Ac − N) for B (x), while B (HCl − N) and B (N) are almost as good. The three quantities using the phenol buffer point, of which only two are given in the table, give definitely larger deviations, while the acetate buffer point is obviously useless.

The variations of (T − W)/B (x) from its mean are probably due to some property of the clay and not solely to chance differences in the amounts of residual bases left in the clay and the experimental errors in the determination of (T − W) and the B's, for the values of $\dfrac{\mathrm{T-W}}{\mathrm{B}\,(y-\mathrm{N})}$, where y is either HCl, the chloracetate buffer, or nothing, are strongly correlated with the quantities $\dfrac{\mathrm{B\,(HCl{-}Ph)}}{\mathrm{B\,(HCl{-}Ac)}}$, $\dfrac{\mathrm{B\,(HCl{-}N)}}{\mathrm{B\,(HCl{-}Ac)}}$ and $\dfrac{\mathrm{B\,(ClAc{-}N)}}{\mathrm{B\,(ClAc{-}Ac)}}$. As an example, the scatter diagram of $\dfrac{\mathrm{T-W}}{\mathrm{B\,(HCl-N)}}$ with $\dfrac{\mathrm{B\,(HCl-N)}}{\mathrm{B\,(HCl-Ac)}}$, which was chosen because it gives the best correlation, is given as fig. 12. In this figure five points have been ringed, namely, two points for the Lower Lias clays, and one for each of the Carse, Kirton-in-Lindsey (dried) and Rothamsted clays. For each of these clays there is a duplicate determination lying nearer the regression line. If these

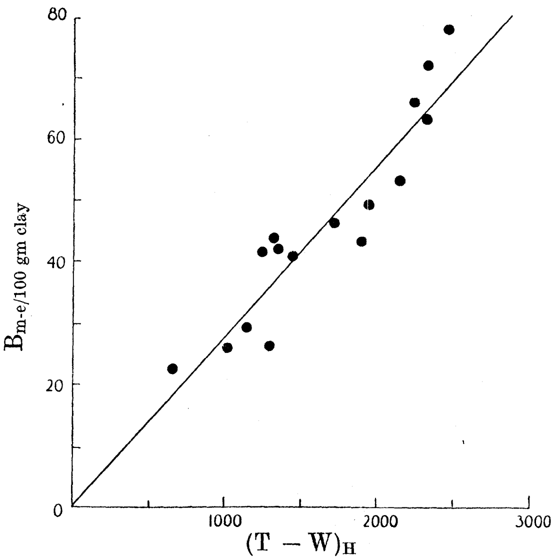

FIG. 10.—Specific volume reduction of hydrogen clays in water to their base holding capacity at p_{H} 7.

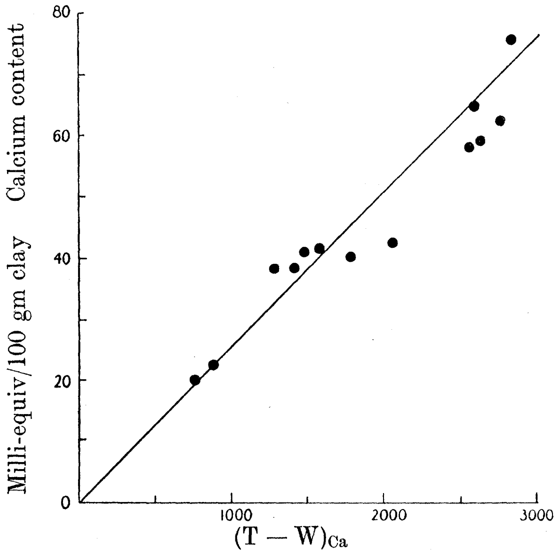

FIG. 11.—Specific volume reduction of calcium clays in water to their calcium content.

TABLE II—(T — L)/B (x) for the Hydrogen Clays

	B(HCl—N) × 10^5	$\frac{\text{B(HCl—N)}}{\text{B(HCl—Ac)}}$	T—W × 10^5	(T — W)/B(x)						(T — L)/B (HCl—N)		
				B(HCl—Ac)	B(HCl—N)	B(HCl—P)	B(ClAc—N)	B(N)	B(P)	Amyl Alcohol	Aniline	Nitro-benzene
Trias (a)	23·8	1·63	733	50·2	30·8	19·1	39·2	34·2	21·1	16·7	22·7	14·2
(b)	23·8	1·63	661	45·3	27·8	17·3	35·4	31·3	19·1	—	—	13·8
Old Red Sandstone ...	31·8	1·64	1,138	58·9	35·8	24·7	45·2	38·6	26·9	—	—	17·9
Rothamsted (a)	39·7	1·70	1,013	43·6	25·6	15·6	36·9	37·1	17·7	—	—	15·6
(b)	39·7	1·70	1,191	51·1	30·0	18·4	43·3	39·9	20·8	—	—	—
Lower Lias Ser. I (a) ...	47·5	1·62	1,679	57·5	35·4	24·9	48·0	39·2	26·5	—	—	8·7
(b) ...	47·5	1·62	1,643	56·1	34·5	24·4	46·9	38·3	26·1	—	—	—
Ser. II ...	51·9	1·80	1,702	59·3	32·9	21·9	45·9	37·5	23·9	—	—	—
Carse, Ser. I	48·1	1·82	1,468	59·8	30·6	21·0	42·6	34·0	22·9	—	—	19·5
Ser. II	60·0	1·80	2,131	64·0	35·5	24·6	48·2	40·7	26·9	29·8	—	—
London I. (a)	47·0	1·60	1,415	48·1	30·1	20·9	43·2	33·8	22·6	21·3	29·6	14·3
(b)	47·0	1·60	1,325	45·1	28·2	19·6	40·4	31·6	21·2	—	—	15·2
London III	49·2	1·35	1,306	35·9	26·5	16·9	43·7	30·4	18·4	25·6	28·6	—
Gloucester (fine)	68·4	1·99	2,240	65·1	32·7	22·9	40·5	36·0	24·4	—	—	10·5
(coarse) ...	69·3	2·06	2,306	68·4	33·3	23·0	40·8	36·8	24·6	—	—	—
Kirton-in-Lindsey (dry) ...	70·6	1·65	2,451	57·2	34·6	25·8	46·7	39·0	27·7	—	—	—
(freeze)	70·6	1·65	2,214	51·6	31·3	23·3	42·2	33·9	25·0	—	23·6	—
Gezira	84·6	1·38	2,328	38·9	27·5	19·5	39·2	36·2	23·5	27·5	—	14·2
Palestine	91·2	1·56	2,459	42·2	27·0	20·0	35·8	31·6	22·3	21·4	—	11·5
Fen	124	2·42	4,645	91·0	37·4	29·1	44·1	42·6	32·2	—	—	10·9
Mean	—	—	—	54·5	31·4	21·6	42·4	36·1	23·8	23·7	26·1	13·9
100S/M	—	—	—	22·8%	11·2%	15·8%	9·1%	9·5%	13·2%	—	—	—

five "bad" duplicate determinations are ignored there is only one point, that for the Old Red Sandstone clay, that lies appreciably off the lines. None of the other possible (T — W)/B (x) values gave such good correlations with any of the B ratios. Thus (T — W)/B (y — N), the mean interaction value of each exchangeable hydrogen ion with water, seems to increase as the B ratios, for example, $\frac{\text{B (HCl — N)}}{\text{B (HCl — Ac)}}$, increase.

From the physical-chemical standpoint $\frac{\text{B (HCl — N)}}{\text{B (HCl — Ac)}}$, namely, the ratio of the calcium which the hydrogen clay holds in a p_{H} 7 buffer, to the calcium which it holds in a p_{H} 4·5 buffer, would be expected to measure the strength of the clay acid, this ratio increasing as the strength of the acid decreases. From this point of view, the mean effectiveness of the hydrogen ions on the clay in reducing the specific volume of the clay in water would increase as the strength of the clay acid decreases, a conclusion not easy to interpret in physico-chemical terms. A second possibility is that as the clay acid becomes weaker the interaction between the molecules of the dispersion liquid and the negative charges on the clay surface becomes stronger. A third possibility is that as the clay acid becomes weaker the pores in the clay crumbs become smaller, so that capillary condensation becomes increasingly more important. This would allow the actual reduction in the specific volume of the clay in water brought about by the hydrogen ions either to be independent of, or to decrease with, the strength of the clay acid, so long as the capillary condensation effect was more or less proportional to $\frac{\text{B (HCl — N)}}{\text{B (HCl — Ac)}}$ for the clay. Unfortunately, so far no measurements of the distribution of pore size in clay crumbs have been made.

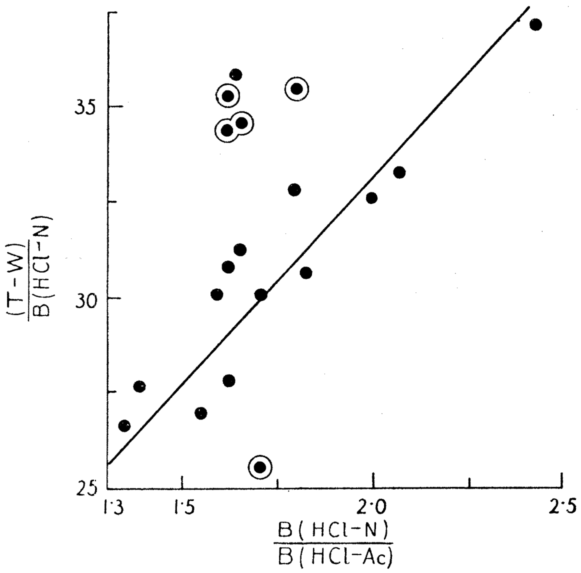

FIG. 12.

The effect of other exchangeable ions held by the clay on the reduction of the specific volume of the clay in water cannot be studied so simply as the hydrogen ion effect, as all other ionic clays contain both exchangeable bases and exchangeable hydrogen, so that the effects of the residual hydrogen on the specific volume is always superimposed on the effects of the other exchangeable cations. This complication will be minimized if all the ionic clays used are in equilibrium with a standard buffer solution of as high a p_H as possible. There are, however, experimental difficulties in preparing pure dry clays in equilibrium with buffers above p_H 7 owing to the formation of insoluble calcium and magnesium carbonates, so that the half-neutralized *p*-nitrophenol buffer of p_H 7 was used as standard for preparing the clays. Further, from the preceding discussion on the hydrogen clays, it appeared that this was about as high as it is necessary to go to eliminate the effect of the residual hydrogen. Although at one stage of their preparation, the clays were in equilibrium with this buffer solution, a certain loss of exchangeable base occurs on removal of this solution, so that the dried clay crumbs do not actually contain sufficient base to be in equilibrium with it, but this loss does not usually exceed 3 milli-quivalents per 100 grams of clay. For these reasons, the influence of the exchangeable bases on the specific volume of the clay cannot be accurately determined. If, as before (T — W) is the reduction in specific volume of the clay in water from that in tetralin, one can, as a first approximation, assume either that it is due to the exchangeable ions actually present and ignore the residual hydrogen, or that it is due both to the exchangeable ions present and to the residual hydrogen, with the implicit assumption that the latter behaves like the base. On the first assumption the mean effect of one equivalent of base held by the clay is (T—W)/B, where B is the amount of base actually held, and on the second is (T — W)/B (HCl — N). Actually the difference between these two quantities is small, and the results are qualitatively the same on either assumption, so that only the results based on the second assumption will be given.

Table III gives the values of (T — W)/B (HCl — N) for all the available non-hydrogen clays which contained nearly sufficient base to be in equilibrium with a p_H 7 buffer, and Tables II and III also give the values of (T — L)/B (HCl — N) for the hydrogen and calcium clays when L is the specific volume of the clay in amyl alcohol, aniline or nitrobenzene. As with the hydrogen clay, (T — L)/B (HCl — N) is fairly constant. The individual variations from the mean can be seen, on plotting out, to be dependent on the clay, and thus on $\dfrac{\text{B (HCl} - \text{N)}}{\text{B (HCl} - \text{Ac)}}$. Naturally, in considering a plot of two quantities such as (T — L)/B (HCl — N) against one another, experimental errors are very serious, for not only are the (T — L)'s and the individual B's subject to appreciable errors, but, since the degree of saturation of the clays with base is variable, this also produces a source of error in the clay.

A certain number of experiments were made with clays holding less base than was necessary to bring them into equilibrium with a p_H 7 buffer. The clays were intended to be in equilibrium with half-neutralized acetate buffer of p_H 4·5 containing N/50 base and N/25 acid, but they were found to have taken up too much base, the extra proportion taken up varying from clay to clay. The results of the comparisons are that for the London, Gloucester, and Lower Lias clays (T — L) seems to be the same for the clay only partially and almost completely saturated up to p_H 7, while for the Kirton-in-Lindsey clay (T — L) increases appreciably between these two levels. The specific volume of the partially saturated clay in tetralin always lies between that of the hydrogen and the fully saturated clay. This indicates that not all the exchangeable ions are equally effective in causing this reduction of specific volume, but that those which can be held in a fairly acid buffer have usually a greater effect.

Table III—(T — L)/B for the Non-Hydrogen Clays

	B(HCl — N) $\times 10_5$	(T — W)/B (HCl — N)				(T — L) B/(HCl — N) for Calcium		
		Calcium	Magnesium	Sodium	Potassium	Amyl Alcohol	Aniline	Nitrobenzene
Trias (*a*)	23·8	31·3	33·6	19·0	15·3	19·5	19·5	17·7
(*b*)	23·8	31·4	—	—	—	—	—	—
Rothamsted	39·7	31·4	—	22·6	16·0	—	—	—
London I (*a*)	47·0	27·2	32·0	16·8	14·8	23·2	23·0	16·0
(*b*)	47·0	30·1	—	—	—	—	—	20·6
London III	49·2	30·1	33·8	20·9	17·6	33·7	23·0	—
Lower Lias Ser. I.	47·5	35·6	36·8	29·0	24·2	—	—	—
Ser. II.	51·9	30·0	—	—	—	—	—	13·7
Carse	48·1	43·0	—	37·4	26·7	—	—	—
Gloucester Ser. I.	64·4	—	—	—	—	—	—	15·6
Ser. II. fine	68·4	38·4	—	35·1	—	—	—	15·2
Ser. II. coarse	69·3	37·0	—	26·0	—	—	—	—
Kirton-in-Lindsey	70·6	39·1	—	30·4	—	—	23·9	—
Palestine	91·2	30·9	31·8	—	—	26·3	—	19·1
Fen	124	40·1	—	—	—	—	—	—
Mean	—	34·0	33·6	26·4	19·1	25·7	22·3	16·9

The mean values of the quantities (T — L)/B(HCl — N) for all the hydrogen clays and all the basic clays nearly in equilibrium with the p_H 7 buffer are given in Table IV. The values are not all directly comparable, however, since the means are derived by averaging over different clays. For example, if the values for the calcium and magnesium are compared for the same clays in water the values are Ca = 31·0 and Mg = 33·6, showing that magnesium gives a definitely larger specific volume reduction in water than calcium. The general order of ion effectiveness is independent of the wetting liquid, and the order of increasing specific volume reduction brought about by one equivalent of exchangeable ion is

K, Na, Ba, H, Ca, Mg.

TABLE IV—Mean values of (T — L)/B (HCl — N) for different exchangeable ions and different liquids

	Potassium	Sodium	Hydrogen	Calcium	Magnesium
Water	19·1 (6)	26·4 (9)	31·4 (20)	34·0 (14)	33·6 (5)
Amyl Alcohol ...	11·3 (1)	11·4 (1)	23·7 (6)	25·7 (4)	36·1 (2)
Aniline	9·5 (1)	10·4 (1)	26·1 (4)	22·3 (4)	33·4 (1)
Nitrobenzene ...	7·3 (1)	8·5 (2)	13·9 (12)	16·9 (7)	20·0 (2)

The figures in brackets give the number of clays used to determine the mean value.

Relative to Ca = 1 for each liquid*

	Potassium	Sodium	Hydrogen	Calcium	Magnesium
Water	0·59	0·76	0·91	1	1·08
Amyl Alcohol ...	0·33	0·35	0·86	1	1·21
Aniline	0·41	0·45	1·17	1	1·46
Nitrobenzene ...	0·46	0·49	0·84	1	1·14
Surface density of charge	0·38	0·55	—	1	1·48

* In this table only results based on direct comparisons with the same clays have been used, so this table cannot be derived from the upper half.

With the exception of hydrogen there is not a single experiment in all those performed in which this order comes out significantly different. The position of hydrogen clay in water is erratic, for although on the average its effect is less than the calcium, in two experiments it comes above calcium and in two below sodium. The position of barium is based on a comparison of only one clay saturated with different exchangeable ions. This order for the activeness of the exchangeable ions in interacting with water has also been found by PATE*, BAVER,† and ANDERSON‡ who measured the heat of wetting of soils and clays saturated with different exchangeable ions, and by JANERT§ who measured the heat of wetting of two of the separated clays here described (Trias, Lower Lias), so that magnesium clays do seem to interact with water or other polar dispersion medium more actively, and potassium clays less actively, than any of the other ionic clays used.

If the mean values of (T — L)/B (HCl — N) for the different exchangeable ions are calculated relative to the calcium ion for the four liquids given in Table IV, these relative values are more or less independent of the liquid, as is seen in the lower half of the table; they are primarily a property of the ion and not of the ion-liquid system. These relative values could probably be predicted from the hypothesis that (T — L)/B (HCl — N), the effectiveness of the ion in reducing the specific volume of a clay in a polar liquid, is proportional to the mean surface density of electric charge on the ion, namely, $ze/4\,\pi r^2$, where

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* 'Soil Sci.,' vol. 20, p. 329 (1925).

† 'J. Amer. Soc. Agron.,' vol. 20, p. 921 (1928).

‡ 'J. Agric. Res.,' vol. 38, p. 565 (1929).

§ 'J. Agric. Sci.,' vol. 24, p. 136 (1934).

r and ze are the radius and the electric charge on the ion. This hypothesis cannot be tested directly since the radii of the ions are not known, but if the radii of the metal atoms in the metal crystal, which are known from X-ray data, are used, a test can be made. In the last row of Table IV are given the surface densities of charge on the different ions relative to calcium calculated in this way, the radii of the atoms used in this calculation being Mg 1·61, Ca 1·97, Na 1·86, and K 2·25A.* These figures are seen to be of the same order of magnitude as the effectiveness of the three metallic ions relative to calcium; thus giving some support to the hypothesis. Exact agreement could not be expected, since the liquids will interact to some extent with the negative charges on the clay surface, and in the above calculation this interaction has all been attributed to the exchangeable ions. No method has yet been used to measure this interaction, which probably varies with the exchangeable ion, for one would expect that the larger the proportion of the exchangeable ions dissociated from the clay surface, the larger will be the number of negative charges on the clay surface that can interact with the molecules of the dispersion medium. Evidence of this effect can be detected in the latter half of Table IV; for example, the sodium and potassium figures are too high as compared with calcium in water, owing to the larger dissociation of these ions from the clay. There is not yet sufficient data on the relative dissociations of the different ions from clays dispersed in different liquids to make possible a quantitative discussion of these discrepancies.

The conclusion of this part of the experimental results is, therefore, that (T — L) is controlled by three main factors: the liquid L used, the amount and the surface charge density of the exchangeable ions on the clay, and by one subsidiary factor, specifying to some extent the shape of the buffer titration curve of the clay or the strength of the clay acid. This factor is probably connected with the interaction between the negative charges on the clay surface and the molecules of the wetting liquid.

The Properties of the Wetting Liquid Affecting the Specific Volume of the Clay

A few experiments were made with other polar liquids to try and discover what properties of the wetting liquid are connected with this reduction of the clay specific volume. For the liquids considered: water, amyl alcohol, aniline, and nitro-benzene, the order of effectiveness of the liquids in decreasing the specific volume of the clay is nitrobenzene least, then aniline, then amyl alcohol, with water greatest; and this order is almost independent of the exchangeable ion on the clay, as is seen from Table IV. Hydrogen clay in aniline is the only definite exception, though possibly magnesium clay in amyl alcohol may be one also. Magnesium clay in aniline is not one, since in the only comparison available (T — W) comes out larger than (T — An). The hydrogen exception is definite, as is seen from all the four available comparisons of the hydrogen clays with calcium clays given in Tables II and III, and is due to a specific interaction

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* Taylor, "A Treatise on Physical Chemistry," vol. I, p. 163 (1930).

between the hydrogen clay and the amine group of aniline, for the same result is obtained if o-xylidine or dimethyl aniline is used instead. Thus, for the separated London III clay, the reduction of specific volume from the tetralin figure of the hydrogen and calcium clays in these three amines is

	Aniline	o-Xylidine	Dimethyl aniline
Hydrogen clay	0·01410	0·01478	0·01295
Calcium clay	0·01135	0·01008	0·00857
Difference	0·00275	0·00470	0·00438

Presumably a simple chemical action is involved: the amine group opens up and is adsorbed to give a substituted ammonium clay, thus

$$\boxed{\text{Clay}} - \text{H} + \text{NH}_2.\text{C}_6\text{H}_5 \rightarrow \boxed{\text{Clay}} - \text{NH}_3.\text{C}_6\text{H}_5.$$

The only factor affecting the liquid order so far recognized is chemical action of the type just discussed. The liquid order is neither in the order of their dielectric constants nor of the quantities μ^2/ε of OSTWALD,* where μ is the dipole and ε the dielectric constant of the liquid, though with the exception of nitrobenzene it is in the order of their dipole moments which is aniline ($1·55 \times 10^{-18}$ e.s.u.), amyl alcohol (1·68), water (? 1·8), nitrobenzene (3·89).† It is not possible at present to account for this discrepancy in the order of nitrobenzene.

Differences in dipole moment between two similar liquids whose molecules are about the same size can nearly quantitatively account for the different reductions of the specific volume of a clay in them below the clay's specific volume in tetralin, for under these conditions the reduction in specific volume is approximately proportional to the dipole moment of the liquid. As an example, the specific volumes of two calcium, two magnesium, a hydrogen, and a sodium London III clay were determined in tetralin, aniline, and dimethyl aniline, and the ratios of the reduction in the specific volume in aniline below that in tetralin to the reduction in dimethyl aniline were:

Hydrogen clay	Magnesium clays	Calcium clays	Sodium clay
1·09	1·12	1·33	1·24
	1·08	1·35	

while the ratio of the dipole moments of aniline and dimethyl aniline is $\dfrac{1·55 \times 10^{-18}}{1·4 \times 10^{-18}}$ $= 1·11$, which is in good agreement with the hydrogen and magnesium figures, but not so good for the calcium or sodium, though the sodium figure is subject to a large experimental error. A further comparison was made of the specific volumes of the three calcium clays, Lias, London I, and Gloucester in the liquids nitrobenzene, chlorbenzene,

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* OSTWALD and ORTLOFF, 'Kolloidzschr.,' vol. 59, p. 25 (1932).

† The dipole moments have, wherever available, been taken from SUTTON, 'Proc. Roy. Soc.,' A, vol. 133, p. 685 (1931).

benzyl chloride, and benzyl alcohol, and the results are given in Table V, where N, ClB, BCl, and B Alc denote the specific volumes of the clays in these four liquids.

Table V—Comparison of the Reduction of Specific Volume of a Clay in two Liquids with the Ratio of their Dipole Moments

	$\frac{T - N}{T - ClB}$	$\frac{T - BAlc}{T - BCl}$	$\frac{T - BAlc}{T - N}$	$\frac{T - BCl}{T - ClB}$
Ca-Lias	3·13	—	1·20	—
Ca-London I	3·02	—	1·14	—
Ca-Gloucester	1·09	2·06	1·31	1·26
Ratio of the dipole ... ... moments of the liquids ...	$\frac{3\cdot93}{1\cdot56} = 2\cdot52$	$\frac{1\cdot6}{1\cdot82} = 0\cdot88$	$\frac{1\cdot6}{3\cdot93} = 0\cdot41$	$\frac{1\cdot82}{1\cdot56} = 1\cdot16$

The determination of the specific volume of the Lias and London clays in benzyl chloride failed owing to a violent reaction which took place between the clays and the benzyl chloride, and which resulted in HCl being given off and a red liquid remaining. It is seen that using the liquids nitrobenzene, chlorbenzene and benzyl chloride, the relative reductions of clay specific volumes in them is of the same order as the ratio of their dipole moments, but the liquid benzyl alcohol lies well outside this group. Thus there appear to exist sets of liquids such that differences between the reduction of the specific volume of a clay in any two liquids in a given set can be accounted for nearly quantitatively by the difference of dipole moment of the molecules of the two liquids. The liquid property that determines to what set a given liquid shall belong is not the molecular size, for benzyl alcohol and benzyl chloride, for example, belong to different sets, but is probably the complex property of the liquid that determines how much molecular association takes place, and how much capillary condensation the liquid will suffer in the clay crumbs.

A few experiments were made to estimate the magnitude of the capillary condensation effects with different liquids by comparing the specific volume of the clay when fully dispersed in the liquid with that of the dried clay crumb wetted with the liquid. If σ_d and σ_c are the specific volumes of a dispersed clay and of the dry clay crumbs, and if m_c grams of liquid suffer capillary condensation per gram of clay crumb, and if v_c is the mean volume of the condensed liquid and v_o of the free liquid, then

$$\sigma_d - \sigma_c = m_c (v_o - v_c) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

provided that (1) the crumbs are completely wetted, (2) the weight of imbibed liquid per gram of clay is the same for both systems, and (3) in the determination of the specific volume the clays have the same weight of residual liquid when weighed dry. The effects of the first two provisos on equation (1) are

(1) suppose a volume v_a cc of air is entrapped in the crumbs per gram of clay, then

$$\sigma_d - \sigma_c = m_c (v_o - v_c) - v_a$$

(2) suppose m_i and m'_i grams of imbibed liquid are held per gram of dispersed and crumbed clay, and let $(v_o - \delta v)$ be the mean specific volume of the liquid represented by the weight $(m_i - m'_i)$, then

$$\sigma_d - \sigma_c = m_c\,(v_o - v_c) - (m_i - m'_i)\delta v$$

showing that σ_c or σ_d is only affected by the imbibitional liquid if there is an appreciable change of volume of the liquid on imbibition.

The chief limitation of the experiments performed is the difficulty in determining the weight of clay in the dispersion. The weight of clay crumbs used for a specific volume determination was taken as the weight of the crumbs after they had been drying in a desiccator over phosphorus pentoxide *in vacuo* for about three weeks. The weight of clay used in the water dispersion was determined by removing the main bulk of the water by evaporation on a water bath, drying at 110° C for 24 hours, and then drying over phosphorus pentoxide *in vacuo* for about a fortnight. Under these conditions it is fairly certain that the moisture content of the two samples of clay will agree within a few tenths of a milligram per gram of clay. The effect of this difference can easily be calculated, for if the dry clay from the dispersion had a moisture content m_r per gram of clay more than the dry clay crumbs, then

$$\sigma_d - \sigma_c = m_c\,(v_o - v_c) + m_r\,(v_o - \sigma)\ \text{(approx.)},$$

where σ is the specific volume of the clay. Thus, if $m_r = 10^{-4}$ grams and $\sigma = 0{\cdot}35$, probably a fair average value, then $\sigma_d - \sigma_c = m_c\,(v_o - v_c) + 3{\cdot}5 \times 10^{-5}$. Hence each tenth of a milligram difference of moisture content per gram of clay between the two dry clays gives a difference of $3{\cdot}5 \times 10^{-5}$ between the two specific volumes.

The results of the comparisons between the specific volumes of deflocculated clays in water and of their crumbs in water are given in Table VI, which shows that σ_c is usually greater than σ_d, so that if much capillary condensation is taking place, this effect is more than counterbalanced by incomplete wetting of the crumbs, or to a smaller imbibition of water by the crumbled clay than by the dispersed clay, or to incomplete drying of the clay before wetting. Since none of the last three factors can be very large, only a little capillary condensation can be taking place.

Table VI—Comparison of the Specific Volume of Deflocculated and Crumbled Clay in Water

	Specific volume of deflocculated clay σ_d	Specific volume of crumbed clay σ_c	Difference $(\sigma_a - \sigma_c)$ $\times 10^4$
Kirton-in-Lindsey NaAc ...	0·3647	0·3656	− 9
NaN ...	0·3605	0·3602	+ 3
Carse Na	0·3792	0·3800	− 8
London I H	0·3547	0·3570	−23
Ca	0·3536	0·3547	−11

Turning to the results of this comparison for non-aqueous dispersions, the technique was very unsatisfactory, since, although the results showed that appreciable capillary condensation appeared to take place if the dried clay crumbs were wetted with ethyl or amyl alcohol, two sources of uncertainty enter rendering the results doubtful. In the first case the density of the free liquid in the clay dispersion always had a higher density than the pure liquid, and in the second the clay crumbs were weighed dry before being wetted with the organic liquid, while the dispersed clay was weighed after it had been dried from the liquid, so that errors of one or two milligrams per gram of clay could easily arise between the comparative weights of the same clay sample, due to different residual liquids on the dry clay. Thus, although capillary condensation probably takes place in clay crumbs in organic liquids, the results give no certain proof that this is so.

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Summary

Clay particles can form strong aggregates, or crumbs, when dry, only if the clay particles are sufficiently small, if there are a sufficient number of small exchangeable ions on the clay, and if the clay has been dried from a dispersion medium whose molecules are polar and sufficiently small.

Individual clay particles have an appreciable interaction with the molecules of polar liquids ; they do not interact, or only slightly with non-polar liquids. On the hypothesis that no differential interaction occurs between the exchangeable ions on the clay and a non-polar hydrocarbon, the magnesium ions on the clay have about seven and the calcium ions about three more molecules of water of hydration than the sodium or potassium ions. Independent evidence is given for this conclusion.

Clays interact with water and organic liquids containing a polar group by causing a contraction in volume of the liquid. For homionic clays, saturated up to p_H 7 with base, this contraction is nearly proportional to the number and mean charge density on the surface of the exchangeable ions on the clay and, to a less extent, it varies with a parameter specifying the shape of the titration curve of the clay.

These results have been interpreted on the hypothesis that cations can orientate polar molecules of the dispersion liquid around them, and this power is proportional to their surface density of charge. This power is also possessed by the free negative charges on the clay particle. When the dispersion liquid has nearly all been removed the cations bind the negative charges on two clay particles together by means of bridges of strongly orientated molecules of the polar dispersion liquid.