

# ANION INFLUENCE ON SOME SOIL PHYSICAL PROPERTIES

*by*

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## ABSTRACT

Addition of HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> to montmorillonite clay and a montmorillonitic soil had little effect on the liquid limit of these materials over a wide range of concentrations. The liquid limit of a kaolinitic soil clay was reduced markedly by both HCl and H<sub>2</sub>SO<sub>4</sub>, whereas H<sub>3</sub>PO<sub>4</sub> decreased the liquid limit value at lower concentrations and increased it at higher ones. These results are discussed in light of the charge variability and of anion retention by the kaolinitic soil.

## INTRODUCTION

Permeability, compressibility, and strength of fine-grained soils are related closely to clay mineral type and to the nature and amount of adsorbed ions and water. In the past, these factors often have been thought of in terms of the Gouy-Chapman diffuse double-layer model of ion adsorption on a charged surface (Lambe, 1953, 1958). Such relationships generally are consistent with the results of research on montmorillonitic clays saturated with monovalent cations (Warkentin, Bolt, and Miller, 1957). Recent work on other ion-clay systems suggests that there are many exceptions to the dicta of the double-layer theory (Aylmore and Quirk, 1959). Indeed, in predominantly kaolinitic soils of widespread occurrence in the southeastern United States, the double-layer theory apparently does not apply in even a qualitative sense. This study is concerned with the effect of anions on the properties of such a soil as compared to some montmorillonitic materials.

An hypothesis that the concentration and species of adsorbed anion will substantially influence the physical properties of acid, kaolinitic soil is reasonable in light of its anion-adsorbing nature. The Gouy-Chapman theory predicts that a clay will adsorb cations and exclude anions. Where this is the case, as with certain montmorillonite-salt solution systems, there is a striking influence of cation species on clay physical properties (Falconer and Mattson, 1933), whereas the anion influence is not great.

In the kaolinitic soil studied, there is an adsorption of anions as well as cations (Thomas, 1960). These differences are shown schematically in Fig. 1.

This diagram indicates that in acid, kaolinitic soils there is an increase in anion concentration as the clay surface is approached. Preliminary data leading to that conclusion have been obtained in this laboratory. Bolt and Warkentin (1958) have shown that the net negative charge on a clay is the sum of the cations held and the anions repelled. In kaolinite, the net negative charge would be approximated by the difference between the

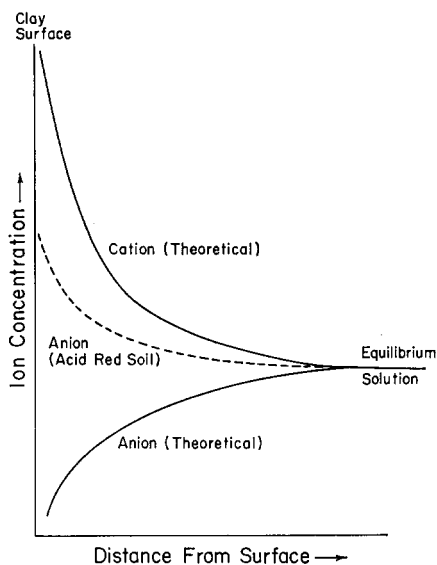


FIGURE 1.—Schematic diagram of theoretical ion adsorption by clay and anion adsorption by acid, kaolinitic (red) soil.

amounts of cations and anions held. In conjunction with this view, the pH of a kaolinitic system has a profound effect upon the net negative charge. Schofield (1939) and Mattson (1927) have shown that oxide-containing kaolinitic soils may actually possess a net positive charge at low pH values. Quirk and Theng (1960) have shown that in montmorillonite, induced changes in negative charge greatly alter the quantity of adsorbed water held by the clay against an applied force. Hence, one would expect the water-holding capacity and allied physical properties of kaolinitic soil to vary with changes in negative charge and in the anion species adsorbed.

## MATERIALS AND METHODS

To test these ideas, a simple laboratory test correlating well with a number of soil physical properties was selected. This is the liquid limit or upper plastic limit test as devised by Atterberg and modified by Casa-

grande (1932). The commonly employed empirical testing procedure defines liquid limit as the water content at which a standard groove of uniform size cut in a soil will close a distance of  $\frac{1}{8}$  in. under 25 blows obtained by dropping the sample cup 1 cm in a standard testing device. Compressibility usually increases with liquid limit (Lambe, 1951). Baver (1948) has noted a linear correlation between liquid limit and moisture equivalent. Lambe (1953) has suggested that the liquid limit approximates an upper limit of "immobilized" water. This is borne out by the data in Fig. 2 indicating

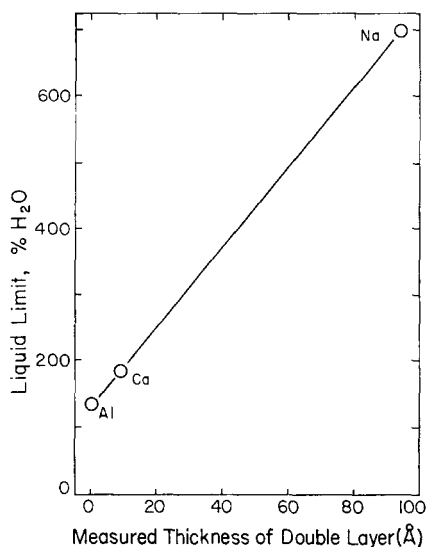


FIGURE 2.—Liquid limit (percent H<sub>2</sub>O) versus measured thickness of double layer for homoionic Wyoming bentonite saturated with sodium, calcium and aluminium.

a close correlation between liquid limit and double-layer thickness in Wyoming bentonite. The liquid limit values for Ca- and Na-saturated montmorillonite are taken from White (1955), and the double-layer thickness was estimated from anion exclusion measurements following the method of Lutz and Kemper (1959).

Materials used in this study were: an acid, Red Podzolic subsoil derived from granite and known as the Cecil series; a montmorillonitic soil derived from diabase and known as the Iredell series; and Wyoming bentonite, a commercial montmorillonite clay. The first two materials were taken from well-known sites in the central Piedmont of Virginia and the bentonite from Upton, Wyoming. The soils were ground and passed through a 40-mesh sieve before using, but no other treatment was imposed. The Cecil soil was essentially Al-saturated, whereas the Iredell was saturated with Mg and Ca. The bentonite was Al-saturated with AlCl<sub>3</sub> and washed free of Cl with

water. Chemical and physical properties of these materials are given in Table 1.

Liquid limit was determined after adding various concentrations of either HCl, H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> and curing for three days at a water content close to the liquid limit. Curing times of more than 24 hr were found to have a negligible effect on the results. Reproducibility of the results (replicate values were generally within 3 percent of one another) was enhanced by employing a single operator and the same equipment throughout the testing program.

TABLE 1.—CHEMICAL AND PHYSICAL PROPERTIES OF EXCHANGE MATERIALS USED

Exchanger	C.E.C.	Exchangeable Cations				Clay Min. <sup>1</sup>			Liquid Limit	Plastic Limit	Plasticity Index
		Al	Ca	Mg	K	K	M	V			
Cecil	4.18	3.54	0.10	0.40	0.14	80	—	20	75.5	43.1	31.4
Iredell	16.74	0	5.20	11.36	0.18	20	80	—	71.5	34.2	37.3
Wyoming Bentonite	90.0	90.0	—	—	—	—	100	—	134	—	—

<sup>1</sup> K = Percent kaolinite and halloysite, M = percent montmorillonite, V = percent dioctahedral vermiculite with interlayer aluminum.

## RESULTS AND DISCUSSION

Figure 3 shows that the addition of sulfate or phosphate ions in the form of acids has no influence on the liquid limit of aluminum-saturated Wyoming bentonite except at very high concentrations. Conceivably, at high concentrations of acid, the hydrogen is replacing much of the aluminum on the exchange complex by mass action. The propensity of phosphate to react with aluminum would enhance such replacement in the case of the phosphoric acid. Because of the looseness with which H<sup>+</sup> is held, the probable result of this replacement is to enhance water adsorption and cause a corresponding increase in liquid limit, as when other monovalent cations are added to montmorillonite (White, 1955).

The influence of acid additions on the liquid limit of Iredell soil, an alkaline-earth-saturated montmorillonitic material, is shown in Fig. 4. Each curve was determined in replicate and each point shown in Fig. 4 is an average of four or five determinations. A considerable scatter of points was given by the replication; far more than with the other materials. The inflections seem to be reproducible, however.

With reference to the effect of H<sub>2</sub>SO<sub>4</sub> and HCl on the liquid limit of the Iredell soil, there are a number of possible reactions, all more or less tenable. The initial decrease in liquid limit may be due to an appearance of trivalent aluminum in the system. This may replace the exchangeable alkaline earths with a resultant decrease in liquid limit (see Fig. 2). Subsequent lowering

of pH may cause the adsorption of hydrogen on the exchange as in the case of the bentonite with a resultant dispersion. The final downswing in

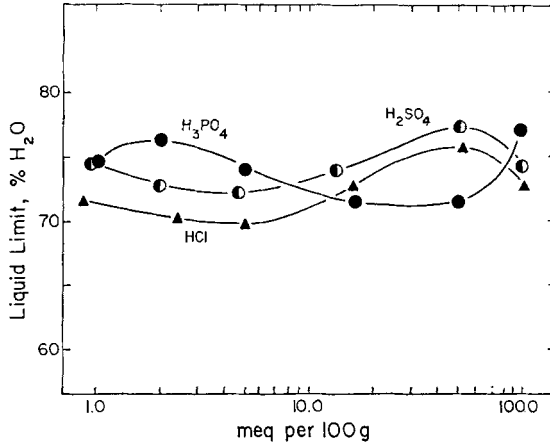


FIGURE 4.--Liquid limit (percent H<sub>2</sub>O) of Iredell soil after additions of HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>.

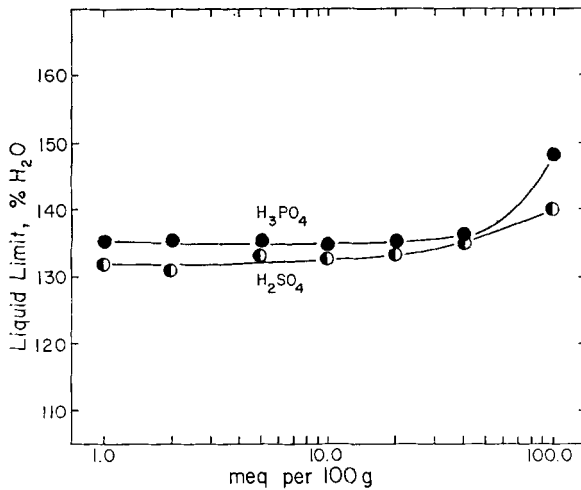


FIGURE 3.--Liquid limit (percent H<sub>2</sub>O) of Wyoming bentonite after additions of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>.

the curves probably represents a procedural difficulty. At such high anion concentrations, oven drying of water content specimens fails to remove the water of crystallization associated with the reaction products and gives erroneously low liquid limit values. The reactions that occur are probably

more a function of cation than anion behavior. The anion effects seem to be restricted to their influence on the availability and replacing power of cations, as in the case of the partially ionized phosphoric acid and the ability of phosphate to remove aluminum from the system.

A sizeable decrease in liquid limit with anion addition to the acid, kaolinitic Cecil soil is shown in Fig.5. In this case replicate determinations agreed very closely. These decreases are difficult to explain on the basis of cation effects alone, but are closely associated with a decrease in net negative charge that occurs when acids are added to the soil. Table 2 shows this change in charge in relation to pH change. Note that with Iredell soil a rise in pH has little effect on net negative charge even though the increase

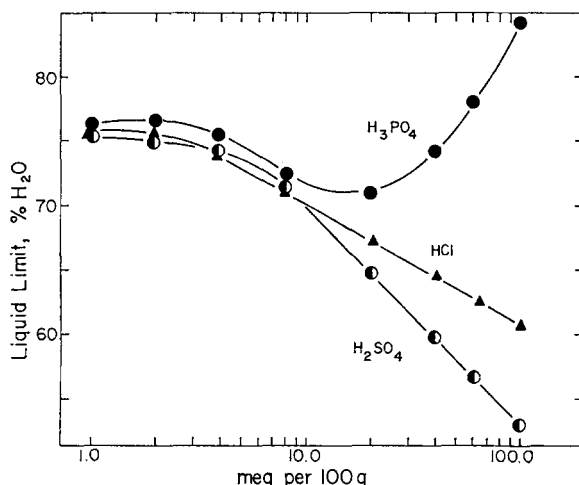


FIGURE 5.—Liquid limit (percent H<sub>2</sub>O) of Cecil soil after additions of HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>.

with Cecil soil is nearly linear. Associated with the kaolinite in Cecil soil are polymers of hydroxy aluminum and iron which exist mostly as clay coatings. Anion adsorption and pH-dependent charge often have been observed for soils containing these polymers (Mehlich, 1950; Mattson,

TABLE 2.—EFFECT OF pH ON NET NEGATIVE CHARGE

pH	Iredell (meq/100 g)	Cecil (meq/100 g)
2.4	20.0	1.40
3.3	—	2.00
4.3	19.9	2.60
5.2	19.9	3.24
6.1	—	4.40

1927). Apparently, the amphoteric nature of the noncrystalline hydrous oxides intensifies the charge variation which is present to some extent in pure kaolinite (Schofield and Samson, 1953).

It is not known whether the negative charge reduction in kaolinitic soils is due to the creation of positive charge sites as proposed by Taylor (1959) or whether it is a result of the suppression of hydrogen ionization from OH groups. The latter theory seems tenable in the case of soils containing an abundance of hydroxy aluminum and iron polymers. Lowering the pH would naturally have the effect of suppressing hydrogen disassociation, but it might also remove the hydroxyl in question from the system by its reaction with hydrogen to form water. In this case, the hydroxyl might be replaced with the added anion forming an aluminum or iron basic salt polymer. Such "ion penetration" has been described by Rollinson (1956) for hydroxy aluminum polymers in solution. Ion penetration, more or less reversible, is plausible for  $\text{SO}_4^{2-}$ , occurs less easily with  $\text{Cl}^-$ , and is difficult to visualize in the case of  $\text{H}_2\text{PO}_4^-$ , although  $\text{H}_2\text{PO}_4^-$  adsorbed by soils has been replaced by  $\text{OH}^-$  (Dean and Rubins, 1947). Still the mechanism of anion adsorption and charge reduction is doubtlessly not as simple in soils as in the case of aluminum hydroxides in solution.

The reduction in charge might itself explain the decrease in "immobilized" water with acid additions since water undoubtedly is attracted to surfaces by electrical forces of various kinds, including electrostatic attraction (Michaels, 1959). An equally good argument may be obtained by resorting to a structural picture. From that point of view it can be concluded that the "edge-face" flocculation described by Schofield and Samson (1953) is destroyed by the addition of large amounts of electrolyte. In this connection, the sharp break in the liquid limit curves (Fig. 5) for Cecil soil occurs at the point at which adsorption of anions is complete, as estimated from conductimetric titration. The effect of the additional anions seems to be that of encouraging a degree of dispersion, although the suspensions become highly viscous. Evidently in this latter condition, either because of some unique structure or because of its virtual "chargelessness," the clay is unable to hold as much water as in its natural condition. The interactions between charge and structure in kaolinitic soils make it almost impossible, at present, to separate these effects.

Whatever the mechanisms whereby net negative charge is reduced and anions are adsorbed, the effect of these reactions is drastically to alter the physical properties of the Cecil soil in contrast to montmorillonitic soils. Also, the amount and manner in which these properties are altered are a function of the nature of the anion. Sulfate, tenaciously adsorbed, causes a greater decrease in liquid limit than chloride, which is weakly adsorbed, although the difference is not great. With phosphate the reaction is more complex, as shown by the upswing in the curve, as though one reaction were

superimposed on another. The secondary and tertiary ionizations of adsorbed  $H_3PO_4$  lead to an increase in negative charge (Coleman and Mehlich, 1948) which apparently enhances the retention of water by the soil. Phosphate also has a propensity to unite with aluminum and iron and form relatively insoluble compounds in a manner not described for sulfate.

### CONCLUSIONS

The scope of this study does not permit definite conclusions about the nature of the physical-chemical system which obtains in acid, kaolinitic soils of the southeast. The results do emphasize the effects of different anions on such soils, in contrast to montmorillonite. This makes it apparent that there is danger in attempting to use theories that apply to monovalent montmorillonite systems to explain the behavior of kaolinitic soils. Clearly, behavior predictions based on the double-layer theory need re-evaluation before application to soils in much of the southern region.

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