

COLLOID CHEMISTRY OF CLAYS

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Colloids are not to be considered as a separate group of substances, but rather as matter in a state characterized by an overwhelming development of surface over total volume. This condition causes matter to exhibit reactivity which is not predictable on the basis of chemical composition alone. This is exemplified by a detailed discussion of the results of chemical analysis of the most important clay minerals, their shape and structure as revealed by x-ray diffraction and electron microscopy, and their colloidal properties. The combination of these findings is used to describe the clay particle as a colloidal micelle. This concept, which has proved to be of greatest value in explaining many phenomena typical of clay minerals, is applied in discussing ion-exchange reactions, plasticity, thixotropy, dilatancy, rheopexy, dispersion, and stream double refraction. The industrial application of these colloidal phenomena is exemplified by a discussion of the use and properties of clay minerals in ceramics, agriculture, soil engineering, oil well drilling, films and plastics, thixotropic pastes, and water softening.

I. INTRODUCTION—THE COLLOIDAL STATE OF MATTER

Many are still under the impression that the term "colloid" refers only to gelatinous substances or to tiny particles being moved around in the medium in which they are dispersed by the Brownian molecular motion. The term "colloid"

was coined by Thomas Graham in 1861. It is derived from the Greek words $\kappa\omicron\lambda\lambda\alpha$ (kolla) meaning *glue*, and $\epsilon\acute{\iota}\delta\omega$ (eido) or $\epsilon\acute{\iota}\delta\omicron\mu\alpha\acute{\iota}$ (eidomei) meaning *like*. Many even still believe that the term "colloid" defines a special group of chemicals, like the words *metal*, *wood*, or *wax*, and that colloid chemistry, therefore, is comparable in its scope to metallurgy or mineralogy. Therefore, it seems necessary to point out at the very outset of a paper dealing with the colloid chemistry of clays that this branch of science is not limited in its scope (like inorganic or organic chemistry) to well-defined groups of chemical compounds, but is the science devoted to the exceptional reactivity and phenomena exhibited by matter if present in the dimensional range from 1 to 500 $m\mu$.

The fact that a substance having one, two, or all three possible dimensions lying within this range will exhibit properties which cannot be predicted or explained by simple analysis or by the reasoning of classical chemistry calls for an explanation. If we take, for example, a cube with 1 mm. edge length, a particle clearly visible in a good microscope, it will have a volume of 1 $mm.^3$, a total surface of 6 $mm.^2$, eight corners, and twelve edges. If we now subdivide it into cubes of 500 $m\mu$ edge length, thus producing particles of a size which has been set as the upper limit of the colloidal range, we shall have produced eight billion cubes. Their combined volume will still be 1 $mm.^3$, but the sum of the now formed surfaces will amount to the staggering figure of 12,000 $mm.^2$ and there will be 64 billion corners and 96 billion edges.

As we further decrease the dimensions of the formed particles, the ratio of volume to exposed surface will become even more pronounced, until we have reached the dimensional range of the individual atoms or ions of which the matter under consideration is composed. Then any differentiation between volume and surface becomes meaningless, at least as far as the chemical compound is concerned. We are then dealing with a gas or a dispersion of dissociated ions, a true solution.

If we look at a model of a bromargyrite (silver bromide) crystal, for example (figure 1), we immediately realize why so much importance must be attached to the surface-to-volume ratio of matter if present in the colloidal state. It is evident that the silver ion (1) should be surrounded by six bromide ions. Only four are visible; the fifth is located behind the silver ion inside of the cube, and the sixth is missing altogether. The corner ion (3) lacks three bromide ions for electrical neutrality. This deficiency, so pronounced in crystalline matter present in a colloidal state of subdivision, as the clay minerals are, explains why they exhibit a reactivity and certain properties which could not be explained on the basis of their chemical composition alone. To achieve neutrality, these ions tend to adsorb positive or negative charges, respectively, from the medium which surrounds them. In this way the so-called diffuse double layer is built up. This layer is composed of those ions which are firmly adsorbed to the surface of the particle and the counter ions which surround the particle at a distance which depends on the strength of their electrostatic attraction and their solvation. The particle plus its diffuse double layer is called a colloidal micelle. Only if the concentration of counter ions is high, owing to an excess of electrolyte

present, or if they are multivalent, will the effective charge carried by the colloidal micelle be neutralized. Nature always tends to produce matter exhibiting least free energy. Therefore, in the above case there will always be the tendency to form the least soluble compound, and should the reaction lead to the formation of crystalline matter, those ions which fit into the crystal lattice will be preferably adsorbed, in accordance with the Fajans-Hahn rule (38).

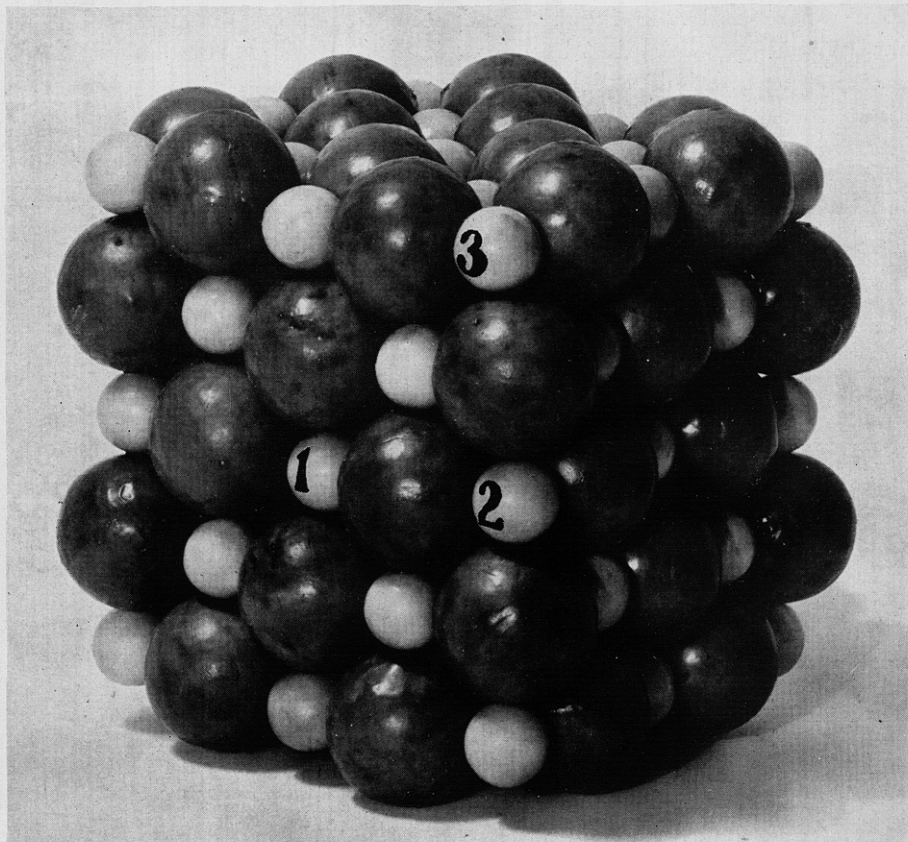


FIG. 1. Close-packed ionic lattice model of a bromargyrite crystal (39). (A detailed description of how to build such close-packed crystal models simply and quickly is given in reference 40.)

If we, therefore, let silver nitrate react with potassium bromide and the concentrations used are not in exactly stoichiometric proportions, then the electric sign imposed on the formed colloidal micelle will depend on the type of ions present in excess. If the reaction is carried out with an excess of silver nitrate, then the residual silver ions will be adsorbed by the unsaturated secondary valencies of the bromide ions located in the surface of the created crystal and positively charged particles will result. If the reaction is carried out with an excess of potassium bromide, the bromide ions will be adsorbed on the silver

ions of the crystal lattice, resulting in negatively charged particles, with potassium ions forming the counter ions (figure 2). The introduction of the concept of a diffuse double layer by Gouy (27) and Freundlich (16) overcame the shortcomings of the double-layer theory originally postulated by Helmholtz (53), which assumed that the surface charge of the colloidal particle is compensated by a counter-ion layer located at monomolecular distance in the dispersion medium (figure 3). The new concept has not only offered a better understanding of the differences between the thermodynamic or galvanic potential (38) and the electrokinetic potential, but has also offered a logical explanation for the fact that the former is independent of ion concentration and solvation, whereas the latter is very much influenced thereby (38).

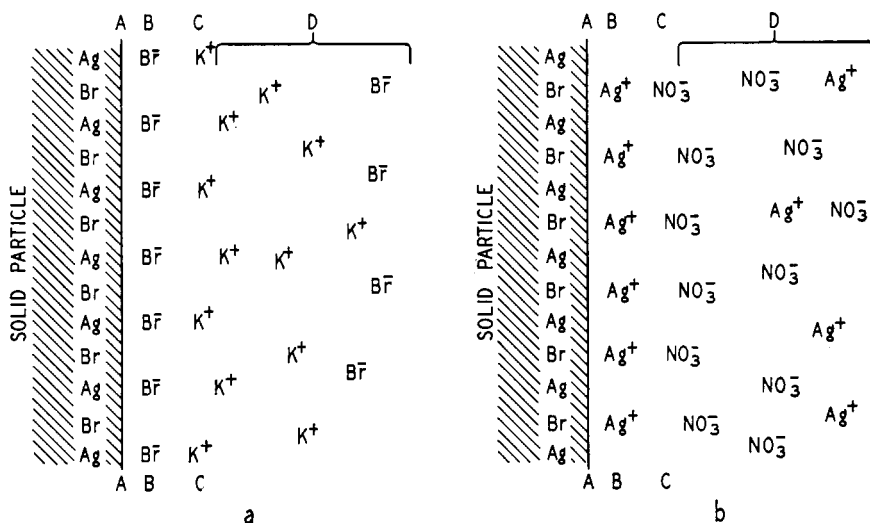


FIG. 2. Arrangement of ions in diffuse double layer surrounding a silver bromide particle. a, negatively charged particle; b, positively charged particle. A, actual surface of particle; B, rigid ionic layer firmly attached to particle; D, diffuse ionic atmosphere in movable part of liquid; C, imaginary boundary between attached non-movable and movable liquid layers (38).

If the counter ions are easily solvated, like sodium, the colloidal micelle will, when placed in water, build a diffuse electric double layer due to the surface dissociation of the counter ions. It is this phenomenon which is most responsible for several of the unique properties exhibited by colloidal clays, and it is this condition of the clay minerals which makes a more fundamental knowledge of their colloid chemistry so important to science and industry.

II. CHEMICAL COMPOSITION, STRUCTURE, AND SHAPE OF CLAY MINERALS

If the most important clay minerals are subjected to quantitative chemical analysis, one finds, as shown in table 1, that this knowledge alone does not suffice to explain either the differences in properties some of the clays exhibit,

although their composition, as found by analysis, is the same, or why some have similar properties, although they differ in chemical composition. Some of the

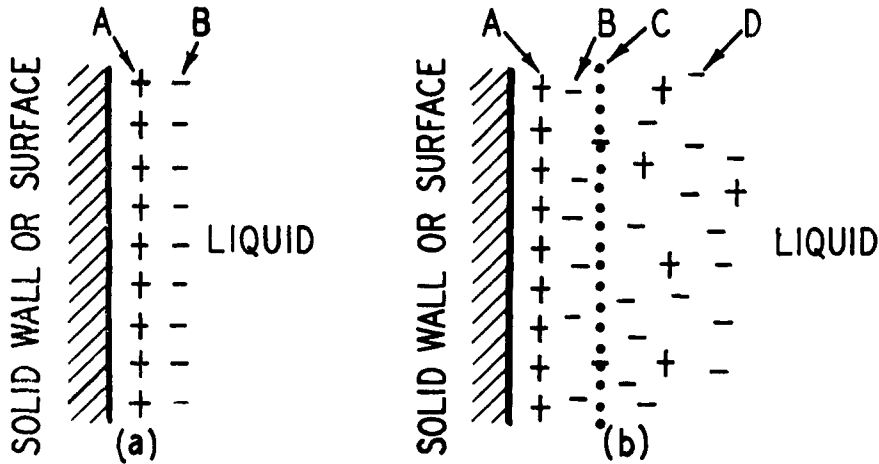


FIG. 3. Double layers. (a) Helmholtz; (b) Gouy-Freundlich diffuse double layer. A, charges firmly adsorbed to particle; Ba, charges in liquid layer; Bb, ions in liquid layer firmly attached to particle; C, thickness of attached layer; D, diffuse ions in movable part of liquid (38).

TABLE 1

MINERAL	CHEMICAL COMPOSITION*	TYPE OF CRYSTAL LATTICE
Kaolinite.....	$Al_4(Si_4O_{10})(OH)_8$	} Kaolinite
Dickite.....	$Al_4(Si_4O_{10})(OH)_8$	
Nacrite.....	$Al_4(Si_4O_{10})(OH)_8$	
Halloysite.....	$Al_4(Si_4O_6)(OH)_{16}$	
Metahalloysite....	$Al_4(Si_4O_{10})(OH)_8$	
Attapulgite (2)....	$Mg_6[Al](Si_8O_{20})(OH)_4(OH)_2 \cdot 4H_2O$	} Montmorillonite
Pyrophyllite.....	$Al_4(Si_8O_{20})(OH)_4$	
Talc.....	$Mg_6(Si_8O_{20})(OH)_4$	
Montmorillonite...	$Al_4[Mg](Si_8O_{20})(OH)_4 \cdot xH_2O$	
Nontonite.....	$Fe_4[Mg](Si_8O_{20})(OH)_4 \cdot xH_2O$	
Beidellite.....	$Al_4[Mg](Si_8[Al]O_{20})(OH)_4 \cdot xH_2O$	
Saponite.....	$Mg_6(Si_8[Mg]O_{20})(OH)_4 \cdot xH_2O$	
Illite (1).....	$K_y \cdot Al_4[Fe_4 \cdot Mg_4 \cdot Mg_6](Si_8 - y \cdot Al_y)O_{20} \dagger$	Illite
Muscovite.....	$K_2 \cdot Al_4(Al_2Si_6O_{20})(OH)_4$	Mica

* Symbols in [] indicate that they may substitute for the symbol written to the left of the bracket.

† According to Grim (28), y varies from 1 to 1.5.

reactions, like gelation, led to the assumption that clays represent matter in the amorphous state. The introduction of two new research tools, the x-ray diffrac-

tion technique and the electron microscope, demonstrated that we are dealing with matter in crystalline form. A careful survey of these facts, coupled with colloid-chemical deductions, soon led to the conclusion that the great variations in properties could be accounted for only by assuming that the clay minerals are composed of comparatively simple building units and that the differences are primarily due to the manner in which these units are put together.

A. X-ray diffraction

Just over twenty years ago Hadding (32) and Rinne (86) proved by x-ray diffraction that clays were not composed of matter in the amorphous state, as had so far been assumed, but were crystalline. Since then our knowledge of the structure of clays has been greatly increased by the application of x-ray diffraction analysis (10, 28, 31, 43, 52, 54, 55, 57, 58, 62, 63, 68, 69, 81). This development, coupled with a more systematic study of the properties exhibited by colloidal clays, has not only led to the establishment of what we today term the clay mineral group, but has also offered a better understanding of some of the phenomena which are so characteristic of colloidal clays and which could not be explained on the basis of purely physicochemical reasoning.




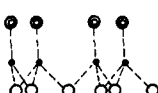
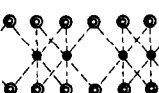
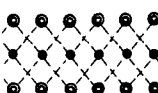
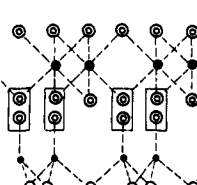
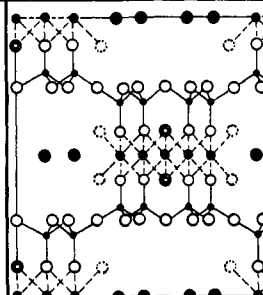
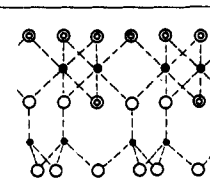
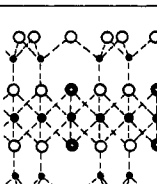
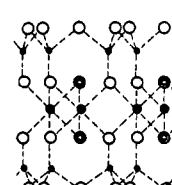
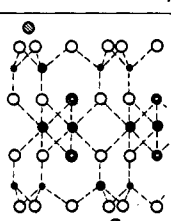
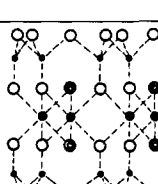
One might compare the structure of the clay minerals with houses built of bricks. One can build houses of different shapes and sizes with the same bricks and mortar. Table 2, based on x-ray diffraction studies, offers the proof for this point of view (39). Columns 1, 2, 3, and 4 give a schematic picture of the bricks used. The mortar used in the building of the clay minerals is the unsaturation of their ultimate building units. For example, a silicon atom will share four electrons with a neighboring atom ($\text{Si} = +4$). An oxygen atom needs two electrons for saturation ($\text{O} = -2$). Therefore, the silicon-oxygen tetrahedron (SiO_4) is not saturated. If several of these tetrahedra combine by sharing oxygen atoms, a chainlike structure results (figure 4). In such a chain, two of the oxygen atoms belonging to every silicon atom remain unsaturated. This deficiency can be compensated for by adsorbing, for example, sodium ions. This will result in a fibrillar aggregate known as sodium silicate or water glass. The fibrous structure and the high degree of hydration of the sodium ion explain the high viscosity exhibited by solutions of water glass. A careful study of table 2 will reveal that all the clay minerals show points of unsaturation at their edges (figure 5) and some, like substituted montmorillonite or mica, even within the crystal lattice. This concept, therefore, offers a simple explanation of many of the properties which are typical of the clay minerals and for which no really satisfactory answer was available on the basis of the chemical composition alone.

B. Electron-microscope studies

Up until only a few years ago our concepts of the shape and the actual dimensions of colloidal clay particles were largely based on deductions derived from combining the findings of chemical analysis, x-ray diffraction patterns, and colloidal phenomena exhibited by the various clay minerals. The development

TABLE 2

Structural data of the most important clay minerals and their building units

1	2	3
 1 O 1 Si 3 O	 3 OH 1 Al 3 OH	 3 OH 1 Mg 3 OH
4	5	6
 4 OH 4 Si 6 O	 6 OH 4 Al 6 OH	 6 OH 6 Mg 6 OH
7	8	
 6 OH 4 Al 6 OH 4 OH 4 Si 6 O	 6 Mg OR Al + 4H ₂ O 2 OH + 4O + 2OH ₂ 4 Si 13 O 4 Si 2 OH ₂ + 4O + 7OH 4 H ₂ O + 5 Mg OR Al 2 OH ₂ + 4O + 1OH 4 Si 13 O 4 Si 2 OH + 4O + 2OH ₂ 6 Mg OR Al + 4 H ₂ O	
9	10	
 6 OH 4 Al 4 O + 2 OH 4 Si 6 O	 6 O 4 Si 4 O + 2 OH 6 Mg 4 O + 2 OH 4 Si 6 O	
11	12	
 6 O 4 Si 4 O + 2 OH 4 Fe ⁺⁺⁺ 4 O + 2 OH 4 Si 6 O	 1 K 6 O 3 Si + 1 Al 4 O + 2 OH 4 Al 4 O + 2 OH 3 Si + 1 Al 6 O 1 K	
13		
 6 O 4 Si 4 O + 2 OH 3 Al + 1 Mg 4 O + 2 OH 4 Si 6 O		<ul style="list-style-type: none"> • - Si ● - Mg, Al, Fe⁺⁺⁺ ○ - O ○ - OH ⊙ - K ● - H₂O ⊙ - OH₂

The schematic drawing in the first column of each section represents the composition of the unit cell of the respective building unit or complete crystal lattice. All atoms have been projected into one plane. The second columns give the number and type of atoms or groups for every lattice plane. 1 = silicon tetrahedron; 2 = aluminum octahedron; 3 = magnesium octahedron; 4 = hydrated silica; 5 = gibbsite; 6 = brucite; 7 = halloysite; 8 = attapulgite; 9 = kaolinite; 10 = talc; 11 = nontronite; 12 = mica (illite); 13 = montmorillonite (substituted).

This table is a rearrangement of illustrations previously published by Grim (28) and the author (39).

of the electron microscope has now put a new research tool in our hands which enables us actually to see, study, and measure particles whose sizes fall within the smallest range of colloidal dimensions (84).

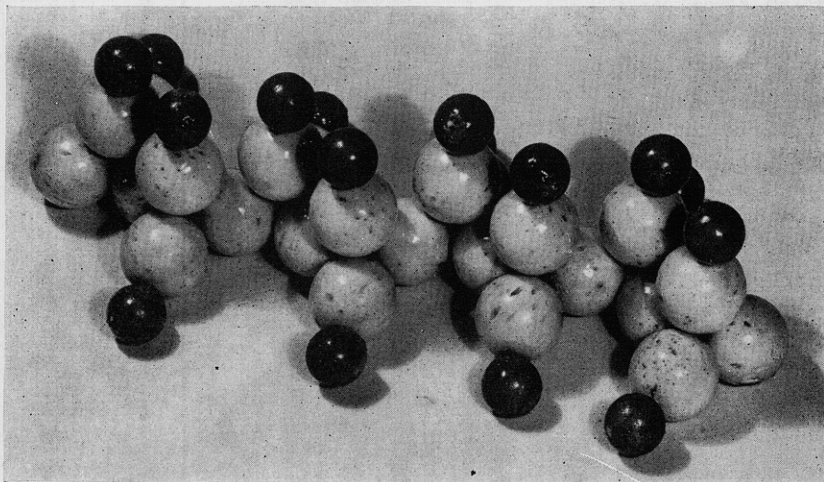


FIG. 4. Model of a sodium silicate chain (theoretical); white balls represent oxygen atoms; black balls, sodium atoms. The silicon atoms are not visible, because they are located in the cavity formed by the four oxygen atoms in tetrahedral position. It is clearly evident that two sodium atoms are needed for the saturation of every tetrahedron (40).

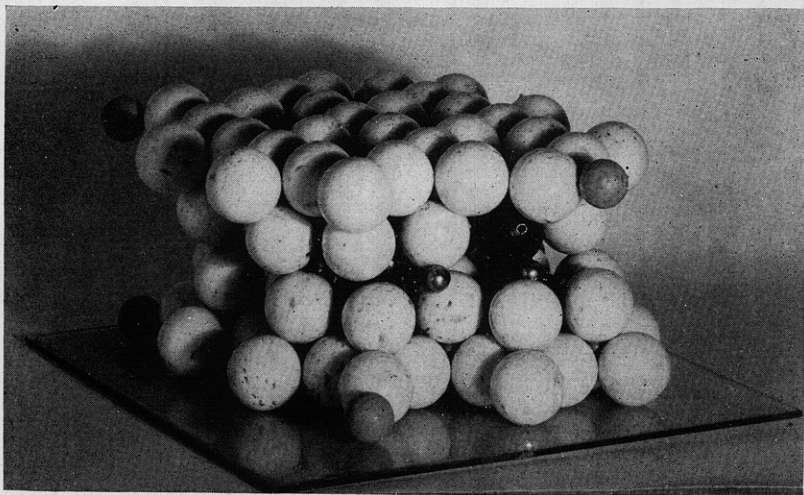


FIG. 5. Model of a single montmorillonite crystallite. The white balls represent oxygen; the black, hydroxyl groups; the small metallic balls, aluminum; the gray balls on the edges, adsorbed cations, for example, sodium (40).

The first to use this new research tool for the study of clays were the Germans, who thereby proved that the particles of bentonite and kaolin actually were of platy shape (1, 2, 11, 12, 13, 14, 79, 84). More detailed studies were carried out

shortly thereafter in this country, and were reported in the excellent summarizing publications of Marshall, Shaw, Humbert (73, 89, 59, 90), and collaborators. Figure 6 shows that the particles of kaolinite are thin plates. Figure 7 shows dickite crystals. Figure 8 represents an electron microphotograph of Wyoming bentonite, which clearly shows that its crystallinity is not as well developed as that of the previously mentioned clays. The clay mineral attapulgite consists of fibrous particles, as shown in figure 9, and the same is the case with the clay mineral halloysite (84, 90).

These findings offer for the first time an explanation for the difference in colloidal properties of the last-mentioned two clay minerals and those exhibited by kaolinite and talc, respectively. The recently made assumption that halloysite and attapulgite should be considered as intermediary products in the

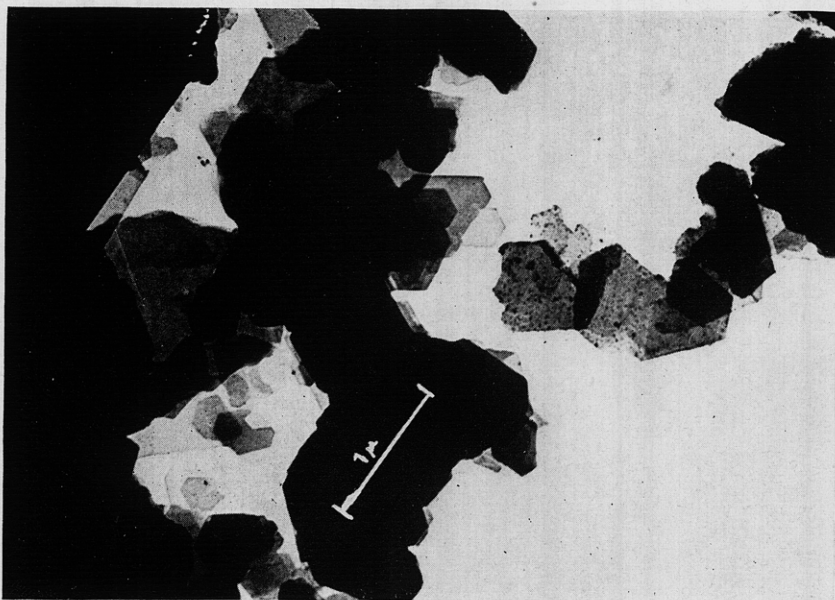


FIG. 6. Electron microphotograph of kaolinite (89)

formation of kaolinite and talc from hydrated silica and hydrated aluminum or magnesium or mixtures of the latter two therefore seems very plausible (28, 39).

III. THE CLAY PARTICLE—A COLLOIDAL MICELLE

The electrical forces associated with a colloidal particle in an electrolytic medium arise from two sources. One set arises from the ions which are rigidly bound to the surface of the particle, and the other is due to the ions of opposite sign which concentrate around the particle in an effort to neutralize its charge. Inasmuch as the particle still carries a net charge, the number of counter ions must be insufficient for neutralization. Since some ions of opposite sign are randomly floating in the dispersion medium, it will carry a charge opposite to that of the colloidal micelle. Figure 10 gives an idea of the relative magnitude

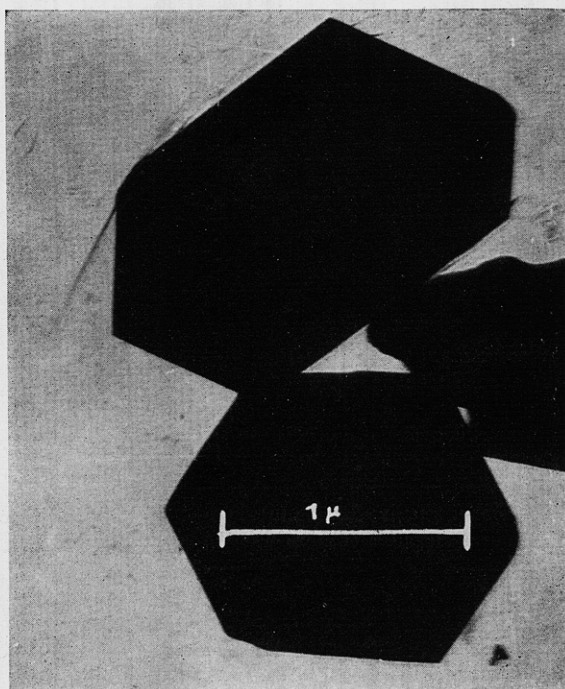


FIG. 7. Electron microphotograph of dickite crystals (59)

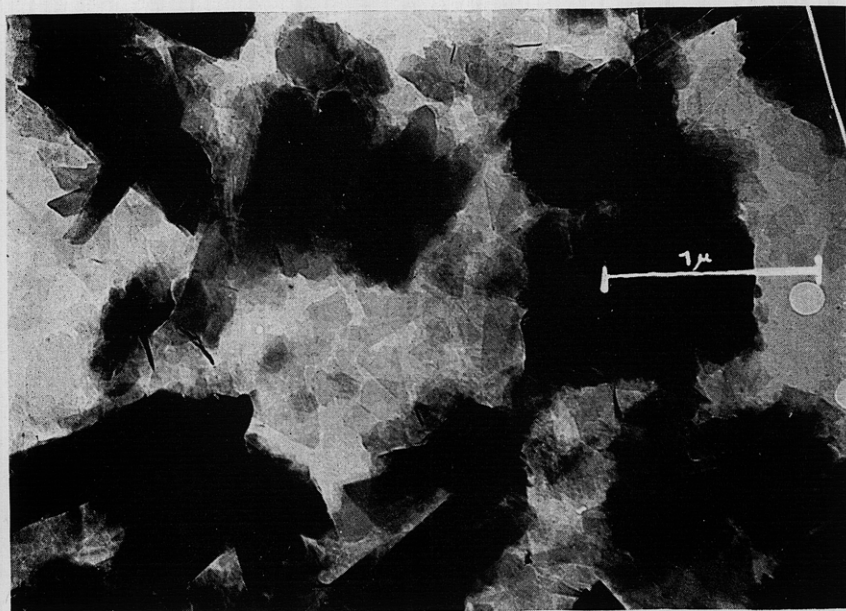


FIG. 8. Electron microphotograph of bentonite (89)

of the electrical forces associated with a colloidal micelle. Line A represents the rate of decline of the electrical forces due to the basic charge of the particle with distance from the surface of the actual particle. Line R shows the decline of the electrical forces associated with the diffuse double layer of net opposite sign. The vertical axis intersecting A and R is the center from which all the ions of the diffuse layer can be assumed to act. If the particle, as is the case with particles of colloidal clays, carries a net negative charge, then curve A would represent the forces of attraction for positive ions in the dispersion medium and curve R the forces of repulsion due to the outer layer of the colloidal micelle toward other similar particles dispersed in the system. We can see that the

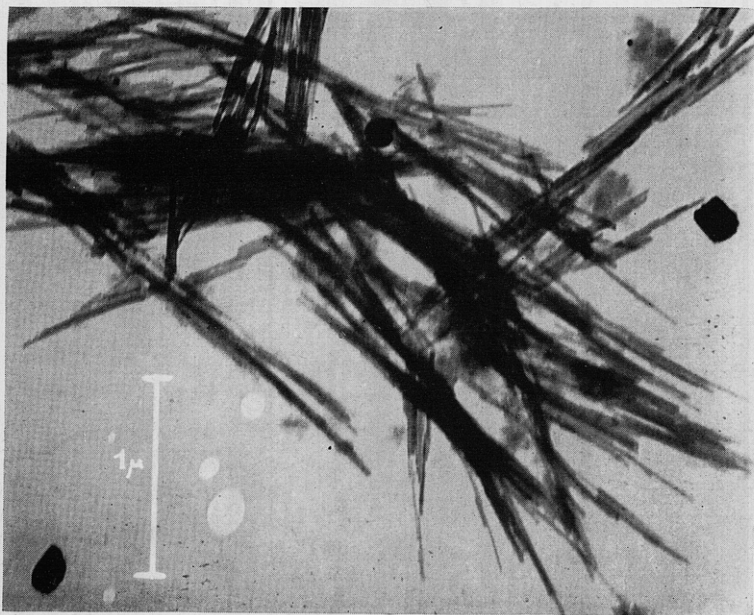


FIG. 9. Electron microphotograph of attapulgite (73)

repulsion forces have the upper hand beyond the diffuse double layer, thus preventing ions of sign opposite to that carried by the particle from coming into close proximity and causing neutralization of the charge and also preventing a close approach by other colloidal micelles of identical composition.

Owing to the adsorption of ions from the dispersion medium by the colloidal particle or to the dissociation of ions from its surface into the dispersion medium, as is typical for clays of the bentonite group, the dispersion medium will possess an excess of ions of a charge opposite to that of the particles. This is evidenced by the phenomenon known as the electroviscous effect. As Smoluchowski has shown, the electroviscous effect is due to a drag caused by the dispersion medium carrying the counter charges moving towards one pole and the dispersed particles moving to the other pole in an electric field (91). This electric field, if of suffi-

cient strength, can cause condensation and orientation of the colloidal micelles (26, 46). This condition will exist until the attraction forces resulting from the charge on the particles and the ions in the dispersion medium are in balance with the forces of repulsion between the ions in the adsorbed diffuse layer and those freely moving in the dispersion medium. Thus, a thixotropic gel (18) will form, but it will immediately revert to a sol if the free movable ions are

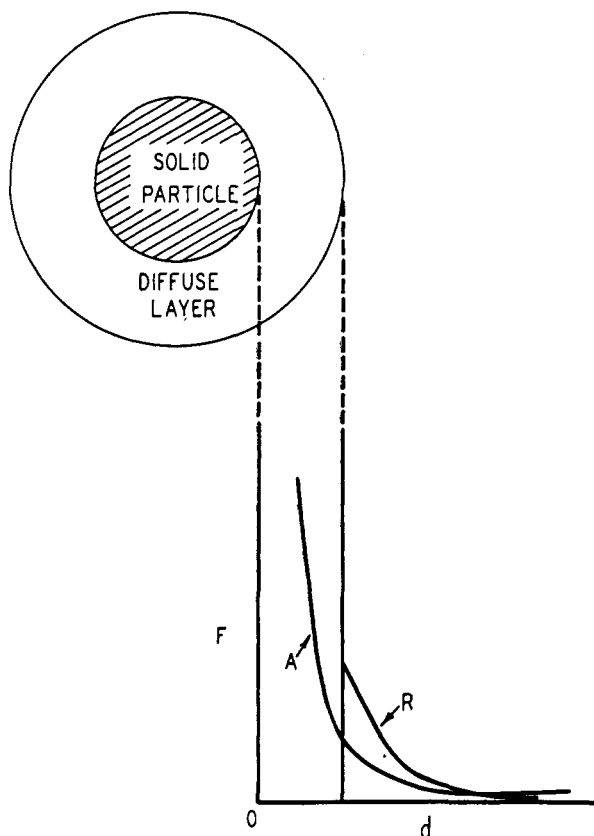


FIG. 10. A schematic picture of the forces associated with the charge of a colloidal particle, the diffuse layer, and any given charge possessing the same sign as the particle, as a function of the distances separating them (46).

redistributed, for example by agitation. If the concentration, valency, or hydration of the counter ions is such that the magnitude of the net charge of the colloidal micelle or the thickness of the diffuse double layer is so reduced that van der Waals attraction forces come into play, coagulation will result, as shown in figure 11.

This concept of the colloidal micelle and of the electric forces connected with it has finally enabled us to offer a simple explanation for many of the properties which are so characteristic of clays and which up to not so long ago baffled the

chemist who could only rely on the results of chemical analysis of a substance. However, before discussing some of them (like plasticity, thixotropy, and rheopecty) in detail, it seems advisable first to lay the foundation for the clay particle

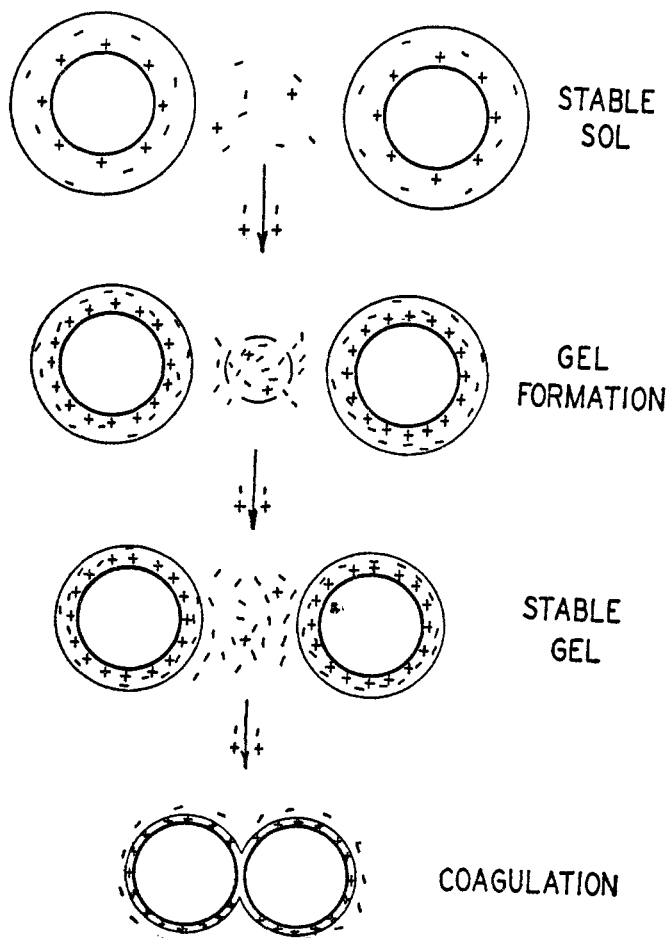


FIG. 11. Coagulation of a colloid by electrolyte. Schematic, simplified picture of the mechanism of gelation and coagulation, showing the formation of ionic fields in the dispersion medium due to preferential adsorption of ions on the surface of the particles. The first step in gel formation corresponds to a thixotropic condition (46).

as a colloidal micelle. Let us, for example, look at a kaolinite particle dispersed in pure water.

Kaolinite, according to its crystallographic classification, is a monoclinic system and therefore displays good cleavage. In the formation of fragments, the fracture occurs along the basal cleavage plane and normal to it, forming thin hexagonal platy particles, but fracture along the cleavage plane does not cause the rupture of primary valence bonds. In a fracture parallel to the *c*-axis of

the crystal unit, however, it becomes necessary to break the bonds between Si and O, Al and OH, or O. (For a schematic drawing of a kaolinite crystal lattice, see table 2, 9.) These broken bonds serve as the basis for the preferential adsorption of hydroxyl ions. The fact, moreover, should not be overlooked that these hydroxyl ions may be bonded by dipolar bonds to the oxygens of the basal silica sheet. Therefore, in order to set up a negative charge on the particle, the location and mechanism of attachment of anions on the surface of the particle are irrelevant. The hydroxyl ions that are thus adsorbed carry with them water molecules (hydration) which make up part of the water hulls. This particle and the cations which swarm about it constitute the Gouy-Freundlich diffuse double layer (figure 12).

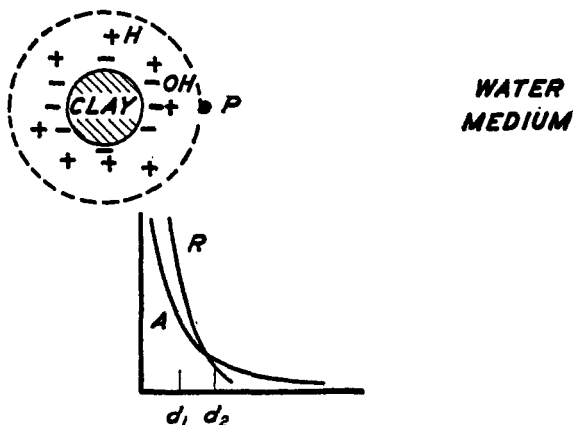


FIG. 12. Schematic representation of the arrangement of the ions associated with a kaolinite micelle in a watery medium (47). The broken circle represents the edge of the diffuse lyosphere associated with the colloidal particle. d_1 represents the average distance from which all of the ions of the diffuse double layer act. At the distance d_2 , P represents the point in the system where the charge associated with the colloidal micelle approaches zero. Curve R represents the decrease of repulsive forces due to the counter ions associated with the diffuse double layer. Curve A represents the decrease of attraction forces due to the hydroxyl ions which give the negative charge to the particle.

If a small trace of an electrolyte (sodium hydroxide) is added to this system, profound changes in the forces connected with the micelle will occur as a result of the preferential ion adsorption on the particle and of the rearrangement of counter charges. Figure 13 shows such an arrangement of the ions of the system and of its attraction-repulsion forces as a function of distance. A considerable repulsion force exists at the edge of the lyosphere, that is, the charge density on the particle and its potential is high, and the entire system is at maximum stability from a colloidal viewpoint because of the presence of large repulsive forces between particles. A kaolinite slip in this state is said to be deflocculated or dispersed (47, 60).

If we now look at the structure of a clay mineral of the montmorillonite group, exhibiting, as is most common, a substituted lattice (table 2, 13) and not the

ideal structure, we find that these substitutions result in establishing net residual negative charges in certain sections of the lattice, which, in turn, cause cation attraction. Sodium is the most common cation found in naturally occurring American bentonites. The crystal units of montmorillonite are only loosely held together by weak O—O bonds. The sodium ions are primarily adsorbed on the surfaces of the silica sheets and to a negligible extent only on the fractures along the *c*-axis. When hydration occurs, these ions pry the particles apart and form double layers of appreciable thickness. The clay exhibits a high degree of swelling. This assumption has been substantiated by x-ray diffraction patterns, revealing a so-called “expanding lattice” along the *c*-axis of the mineral (39).

In the formation of bentonite particles fractures parallel to the *c*-axis, similar to those occurring in the kaolinite crystal, seldom take place. On these surfaces

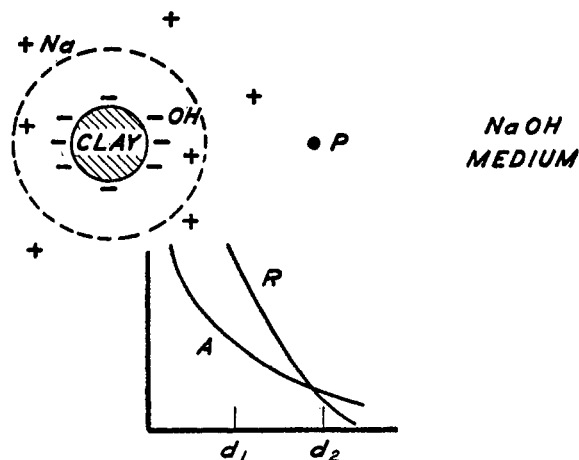


FIG. 13. Schematic representation of the arrangement of the ions associated with a kaolinite micelle in an alkaline medium (47.) (For an explanation of the lettering, see figure 12.)

a diffuse double layer, identical with that obtained with kaolinite, can theoretically be formed, that is, first a layer of preferentially adsorbed hydroxyl ions and then the counter ions in a diffuse arrangement.

With this as a basis, we can now discuss the most important properties of the clay minerals far more intelligently than has so far been possible and thereby demonstrate the importance colloid chemistry has in any field of science and technology in which clays are encountered or used.

IV. COLLOIDAL PHENOMENA AND PROPERTIES OF CLAYS

On the preceding pages the attempt was made to familiarize the reader with the real meaning of the term “colloidal state of matter” and to offer as simple as possible an explanation why matter, if present in that state, will exhibit properties quite unique to that condition. The main purpose of this was to explain

why a clay particle—not only because of its size and shape, but also because of its chemical composition—must, when dispersed in water or a solution of electrolytes, be regarded as a colloidal micelle. In the following pages proof for the importance of colloid chemistry in explaining some of the phenomena and properties which are so characteristic of clays will be offered.

A. Ion exchange¹

The most important and interesting phenomenon exhibited by those clay minerals which will in contact with water form a colloidal micelle is the ion-exchange reaction. This reaction was originally recognized by Thompson in his investigation on the properties of soils (95); the first systematic work upon it was done by Way (99).

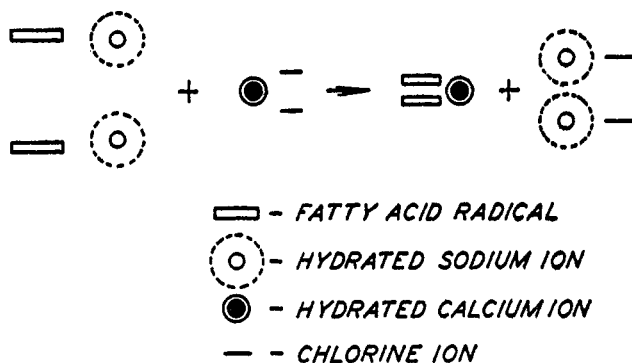


FIG. 14. Schematic representation of the formation of a less dissociated and less soluble soap by cation exchange.

As has been shown, the ultimate clay crystal carries a net negative charge. This charge is either the result of anion adsorption onto its surface, or it can also be due to an unbalanced crystal lattice. Whatever the basic cause may be, one can picture the individual ultimate clay particle as a very complex anion. Therefore, to balance its charge, the particle will have the tendency to adsorb the necessary number of cations available in its environment. When such a clay particle is then again dispersed in water, these cations will hydrate and, depending on their valency and degree of hydratability, dissociate to a certain distance from the surface of the particle and thereby build up a diffuse electric double layer and give rise to the formation of a colloidal micelle. Therefore, one may compare the suspended clay particle with a dissociated electrolyte, the size of one of its ions falling within the colloidal range of dimensions. A similar condition exists in the case of soap, where the sodium ion, owing to its hydration,

¹ After this article had gone to press there appeared a paper entitled "Base Exchange of Crystalline Silicates" by H. B. Hendricks (*Ind. Eng. Chem.* **37**, 625 (1945)), which deserves special attention from those who are interested in the correlation of base exchange with the crystal structure of clay minerals.

will dissociate from the fatty acid ion when the soap is brought into contact with soft water. If, however, hard water is used, then the divalent and less hydrated calcium ions contained therein will exchange for the sodium ions and form the far less soluble calcium soap, as schematically shown in figure 14.

By exactly the same mechanism, the counter ions of the clay particle can be exchanged with ions from the dispersion medium, if the resulting micelle will have less tendency to hydrate and carry a lower charge, or both (74, 100) (figure 15). This reaction is, of course, the more pronounced the more ions of a high

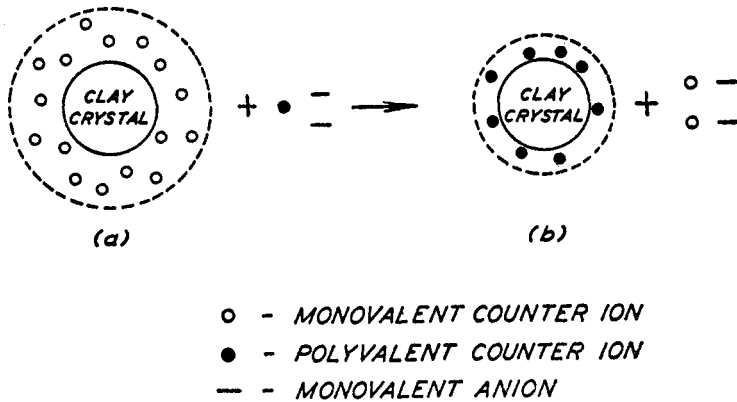


FIG. 15. Schematic representation of the base-exchange reaction of a clay micelle. (a) Clay particle with diffuse electric double layer formed by dissociation of adsorbed counter ions; (b) clay particle with diffuse electric double layer reduced in thickness owing to the exchange of the highly solvated monovalent cations for less solvated polyvalent cations.

TABLE 3 (43)

MINERAL	BASE-EXCHANGE CAPACITY
	<i>milliequiv. per 100 g. of clay</i>
Montmorillonite.....	60-100
Attapulgate.....	25-30
Illite.....	20-4
Kaolinite.....	3-15

degree of hydration are present in the clay under investigation. The magnitude of this ability to adsorb cations, therefore, depends on the structural configuration of the nucleus of the colloidal clay micelle. It is expressed in milliequivalents of cations per 100 g. of clay. Table 3 gives the exchange capacities for the most important clay minerals.

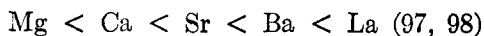
However, by the same reasoning, clays can also adsorb anions where net positive charges are set up in the crystal lattice, or where the hydrogen of a hydroxyl group is exchanged for a stronger ion, like PO_4^{--} (92).

Quite generally, one can state that ion exchange will follow the Hofmeister or lyotropic series, at least for cations, i.e., the higher the atomic weight of an

ion, the more firmly it will be held by the exchanger. Therefore, the exchange reaction for monovalent ions will follow the series



and for multivalent ions the series



Besides valency and hydration, the size of the exchanging ion is also important, because it is difficult to replace ions which have an apparent diameter of at

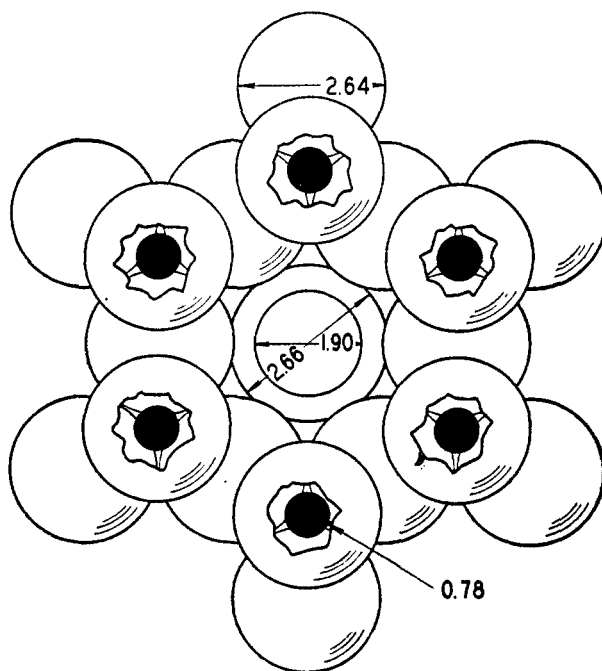


FIG. 16. Hexagonal arrangement of silicon-oxygen tetrahedra in a silica sheet (schematic). The top oxygen atoms have been cut open to show the location of the silicon atoms. The large circle in the center space with a diameter of 2.66 Å. corresponds to the diameter of a potassium atom, the smaller one to a sodium atom. The actual dimensions in Ångström units (1 Å. = 0.1 millimicron) for the different atoms are indicated on the drawing (39).

least 2.64 Å., which is the diameter of the circle one can inscribe into the hexagonal net of oxygen atoms forming the silica sheet (39, 43, 64) (figure 16).

From this one can immediately see why even the dry potassium ion having an apparent diameter of 2.66 Å. is so difficult to replace, and why clays like mica and illite are not readily affected by water. The size of the hydrated exchanged ion is, of course, of importance in regard to the thickness of the formed diffuse double layer, and it will also control the equilibrium exchange, as shown in figure 17.

Base exchange is not, as was assumed for a long time, limited to inorganic cations. Organic cations can be introduced just as well, if they are hydrophilic.

This fact also is the basis for the development of water-resistant clay films, the production and use of which will be discussed in more detail later (41, 43).

The importance of the ion-exchange reaction of clays in explaining the high plasticity, dry strength, thixotropy, dilatancy, and many other properties which are so characteristic of the clay minerals must by now be quite evident, but will become even more so if the reader bears the mechanism of this phenomenon in mind when going over the following sections.

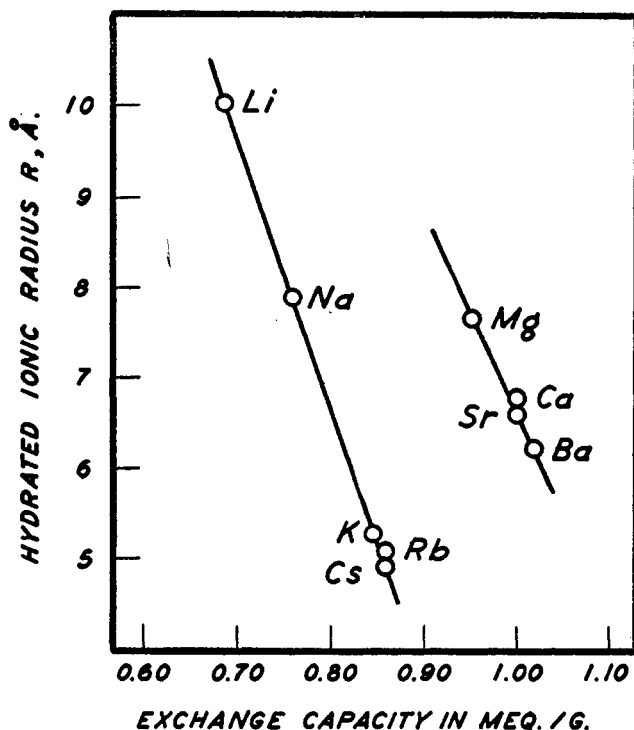


Fig. 17. Radii of hydrated ions versus exchange capacity at equilibrium (77)

B. Plasticity

In contrast to a system exhibiting truly viscous flow, one which exhibits truly plastic flow calls for the initial expenditure of force before shear occurs. Therefore, in a truly plastic system some force must first be overcome, which, owing to its influence, prevents the proportional relationship of applied force to shear, as is typical for a truly viscous system. The point at which this relationship is finally established is known as the "yield point". It constitutes the customary measure for plasticity. In clay systems, plasticity is the result of the attraction and repulsion forces set up between the colloidal clay micelles and the ions in the dispersion medium.

In the specific case of kaolinite, hydroxyl ions may be preferentially adsorbed (60). The kaolinite particle consequently takes on a net negative charge, and

an attraction is set up between the kaolinite particle and any positive charges in its environment. The repulsion forces that are associated with the colloidal micelle (46) originate with the counter ions which swarm about the colloidal particle in an effort to neutralize its surface charge. These counter ions complete the diffuse double layer, and, although they may be any cation, the amount of active repulsive force in the system depends on the type of cation serving as the counter ion (60).

In the preceding discussion, the importance of the attraction and repulsion forces connected with the structure of colloidal micelles has been pointed out. It is, therefore, possible to discuss the cause of plasticity on the basis of these fundamental principles.

The most important single cause for the yield value of the kaolinite-water systems probably is the diffuse electric double layer associated with the solid particles or nuclei.

Kaolinite, according to its crystallographic classification, belongs to the monoclinic system and it displays good cleavage. In the formation of fragments, the fracture occurs along the basal cleavage plane and normal to it, forming thin hexagonal platy particles, but fracture along the cleavage plane does not cause the rupture of primary valence bonds. In a fracture parallel to the *c*-axis of the crystal unit, however, it becomes necessary to break the bonds between Si and O, Al and OH, or O (39, 81). These broken bonds serve as the basis for the preferential adsorption of hydroxyl ions (39). The fact, moreover, should not be overlooked that these hydroxyl ions may be bonded by dipolar bonds to the oxygens of the basal silica sheet. In order to set up a negative charge on the particle, the location and mechanism of the attachment of anions on the surface of the particle is, as has been previously stated, irrelevant. The hydroxyl ions thus adsorbed carry with them water molecules (hydration) which make up part of the water hulls. The particle and the cations which swarm about give rise to the Gouy-Freundlich diffuse double layer.

The crystallographic arrangement of the ions or atoms in certain substances causes the ions located on the surface, corners, and edges to be unsaturated and gives rise to the preferential adsorption of oppositely charged ions (39). A consideration of the plastic properties of any mineral must, therefore, include a careful analysis of the characteristics of the diffuse double layer formed by the particular substance under question. This analysis is highly important because, if the plasticity of a substance depends on the particular attraction forces between unsaturated valence bonds and the adsorbed ions, complete information about all of the ions in the system should furnish data relating to its plastic properties.

The size of the particle exhibiting plasticity is of interest only insofar as it affects the attraction forces between the adsorbed ions and the unsaturated valence bonds of the particle. Inasmuch as the limit of size assigned to a colloidal particle is arbitrarily set at a value where surface forces predominate, it is this size which governs the dimensions of the particles exhibiting plasticity. According to the preceding statements, for example, plastic flow and plasticity

of suspensions are colloidal phenomena, and particles of colloidal dimensions, therefore, are obviously necessary in the system to permit this property or any colloidal property to manifest itself. Depending, then, on the nature of the material (a shape factor must be introduced), the size of the particle and its relation to the total surface area must be considered.

In the case of kaolinite, an average equivalent spherical diameter of less than 4 microns appears to be necessary before plastic properties become evident (100). Such an equivalent size is far above the arbitrary value set for the upper limit of the colloidal range. Kaolinite particles, however, exist in the form of plates, their thickness being well within the colloidal range. The surface along this particular dimension is sufficiently active to cause the colloidal phenomenon of plasticity to begin to manifest itself.

In the case of fibrillar particles, two dimensions may lie within the colloidal range, but the third one need not. In the corpuscular system, all three dimensions of the particle must be within the colloidal range. The factor of size is, therefore, important, and careful consideration must be given to this variable in any study of colloidal characteristics.

The plastic properties of the clay mineral attapulgite have been found to be in full accord with its fibrous, crystalline structure (74).

The term "bentonite" refers to a rock formation composed largely of members of the montmorillonite group of clay minerals. Most of these minerals, furthermore, do not, as already pointed out, conform to the ideal structure, and lattice substitutions frequently occur. The crystal units of montmorillonite are only loosely held together by weak O—O bonds. The sodium ions are primarily adsorbed on the surfaces of the silica sheets. When hydration occurs, these ions pry the particles apart and form double layers of appreciable thickness. The clay exhibits a high degree of swelling.

In the formation of bentonite particles, fractures parallel to the *c*-axis, similar to those occurring in the kaolinite crystal, seldom take place. On these surfaces a diffuse double layer, identical with that obtained with kaolinite, can theoretically be formed, that is, first a layer of preferentially adsorbed hydroxyl ions and then the counter ions in a diffuse arrangement. The presence of hydrogen as the counter ion, all other factors being constant, would give the greatest attraction force at the edge of the water hull, and therefore the greatest plasticity. The least plasticity should be exhibited when sodium ions serve as counter charges for the preferentially adsorbed hydroxyl groups.

Although no detailed systematic studies of the plasticity of bentonites have been reported, it is reasonable to assume that their results will be similar, at least in principle, to those for kaolinite. It must naturally be remembered that the particle structure, location, and cause of net charges on the particle surface and, consequently, the distribution of counter ions are not the same, and that the average size of the bentonite particles is smaller than those of kaolinite. There seems to be sufficient evidence, however, to assume that a hydrogen bentonite will be the most plastic and a sodium bentonite the least plastic.

C. Dispersion

The development of the concept which considers the individual clay particle as a colloidal micelle has given the real basis for the understanding of the reactions which control flocculation, deflocculation, and dispersion of clay suspensions. From the foregoing discussions it is evident that these phenomena depend on the ion distribution in the diffuse double layer surrounding every particle or, to state it more concretely, on the ζ -potential of the clay micelle. Thus, any ion which will cause a reduction in the electrokinetic potential will tend to decrease the stability of the suspension, whereas ions which aid in building up the diffuse ion double layer will act as stabilizing or dispersing agents. This approach can best be explained by applying schematic drawings, as in figure 18 (15). Sodium phosphates, tannates, and several other organic sodium compounds have proven to be very effective deflocculating or dispersing agents.

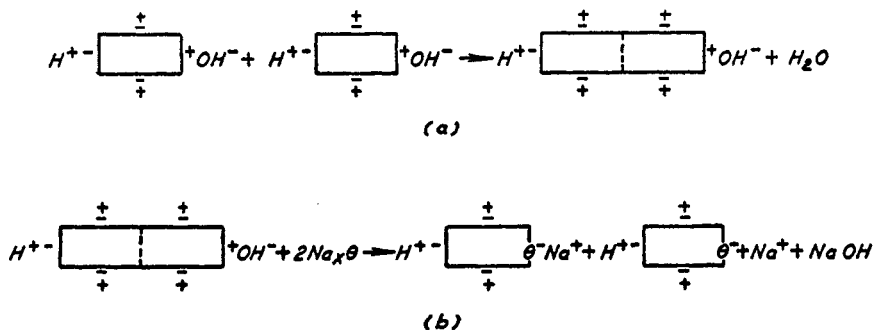


FIG. 18. (a) Condensation of kaolin particles. (b) Dispersion of flocculated clay particles by the addition of a dispersing agent, represented by $\text{Na}_x\theta$. (Na = sodium; θ = anion.)

D. Dilatancy

This phenomenon was first discussed by Osborne Reynolds (85), when he described how quicksand or an ocean beach at ebb tide will appear moist when at rest, but become quite dry and crumbly when trodden upon. Very little attention was paid to this phenomenon, which frequently has been confused with thixotropy, until it was found that it is not limited, as originally assumed, to spherical particles like starch (80), but that particles of platy shape, like very finely ground mica (48), quartz, glass, porcelain (19), or powdered slate (21) also give rise to a dilatant system, if the suspension is subjected to rapid deformation by stirring, application of pressure, or the like (48).

Dilatancy has so far only been observed with lyophobic suspensions, and the lower the stability of the dispersion, the more pronounced it becomes. Furthermore, only such systems have exhibited dilatancy whose particle size is not smaller than the upper limit of the colloidal range of dimensions. The best explanation for this phenomenon is the one offered by Freundlich (19). When the system is at rest, the particles are independent of each other, thus resulting in

closely packed sediments or gels. If an external force is applied to such a system, it causes unequal distribution of the particles and eventually agglomeration results. Local piling up and the formation of cavities in other places occur. The free dispersion medium is sucked into these, and the entire system will behave as if it were dry (figure 19). When the force is removed, the particles will again take up their equilibrium position in accord with their electrokinetic condition, and the system will revert to its uniform, moist or wet appearance.

Dilatancy can be destroyed either by reducing the concentration of the dispersed phase, or by increasing the ζ -potential of the dispersed particles, or by coating them with a protective colloid. A better understanding of this up to now rather neglected phenomenon will assist in reducing many so far unexplained failures in any scientific work or industrial process in which hydrophobic clay suspensions are used or encountered, as for example in ceramics, oil well drilling, and soil conservation.

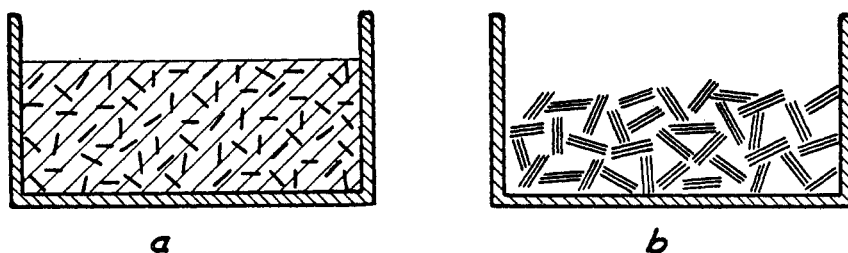


FIG. 19. Dilatancy: (a) system at rest; (b) system when subjected to pressure or mechanical agitation.

E. Thixotropy

In 1923 Szegvari and Schalek noticed that a colloidal iron oxide sol will set to a gel upon the addition of electrolytes and that this gel can be liquefied simply by shaking. If then allowed to rest it will again set to a gel (93). Péterfi (83), who somewhat later noticed the same phenomenon in cell protoplasm, coined the name, deriving it from the Greek words $\theta\acute{\iota}\xi\iota\varsigma$ (thixis) meaning *the touch*, and $\tau\rho\acute{\epsilon}\pi\omega$ (trepo) meaning *to change*. H. Freundlich, to whom we owe the first and only existing summarizing treatise of this interesting colloidal phenomenon (18), was also the first to find that bentonite, if dispersed in water at a concentration of about 12 per cent, will give a thixotropic gel (17). Shortly thereafter it was discovered that dialyzed bentonite did not exhibit thixotropy, but that this phenomenon could be induced by the addition of alkali hydroxides to the dispersion medium. More detailed discussions of the effect of electrolytes on the thixotropy of bentonite suspensions of high concentration have been published by Freundlich and his coworkers (24, 25).

The first ultramicroscopic study of thixotropic bentonite sols was made by Hauser, who also proved that a thixotropic bentonite gel can be obtained at concentrations of only 0.26 per cent if the right amount of electrolyte is added.

Furthermore, it was demonstrated that, upon addition of electrolyte to a dialyzed bentonite sol, first the translatory and then the rotary component of the Brownian molecular motion stops (34). These results made it probable that particle size and the corresponding development of diffuse ion double layers influenced thixotropic gelation. This was proven by subjecting dispersions of crude bentonite to fractional supercentrifugation (50) and determining the thixotropy of various particle sizes. It could be shown that thixotropy became more pronounced the smaller the particle size. Particles with an average equivalent spherical diameter of $15 \text{ m}\mu$ would yield a thixotropic gel at concentrations as low as 0.05 per cent (51). This, coupled with ultramicroscopic (42) and more recently electron-microscopic observations and the fact that no change in volume can be detected when the sol changes to a gel, that preferentially anisometric particles yield truly thixotropic systems, and finally that the electrokinetic condition of the colloidal micelle is of primary importance, permit us to draw the following conclusion: Clay dispersions exhibiting thixotropy are characterized by such distribution of ions in their diffuse double layer, resulting either from adsorption by added electrolytes or from surface dissociation, that the particles with their solvated hulls will, if left undisturbed, take on equilibrium positions. However, if disturbed, the solvated hulls are disrupted and the particles can then freely move around. This concept is substantiated by the sudden change in light transmission when a bentonite sol sets to a gel (35), and is also in line with Langmuir's mathematical treatment of thixotropic systems (65), which concludes that the particles in the gel are placed like ions in a crystal and lie at considerable distance (up to 5000 \AA .) from each other. They are locked into their places by the balance of far-reaching attraction forces and appropriate repulsion forces set up by the interplay of the surface ions of the clay crystal and the free ions in the dispersion medium (19). This theory, based on actual observations, was, therefore, substituted for the previous so-called mechanical theory, which assumed that the clay particles touch each other in completely random, three-dimensional orientation (6).

Thixotropy has also been found with Solnhofen slate, famous for its petrifications of such delicate structures as jellyfish (21). The thixotropy of quicksand must also be attributed to the presence of colloidal clays of high base-exchange capacity (22).

F. Rheopexy

The phenomenon of rheopexy (derived from the Greek words $\rho\acute{\epsilon}\omega$ (reo) meaning *to flow*, and $\pi\eta\kappa\tau\acute{o}\varsigma$ (pectos) meaning *solidified or curdled*) has so far only been observed with a few systems which are known to be thixotropic. Freundlich and Juliusburger (23) found that the setting time of thixotropic suspensions of colloidal gypsum and of vanadium pentoxide could be drastically reduced if the test tube containing the sol was slowly rolled back and forth between the palms of the hands. The same result was obtained by tapping the tube on a table at regular intervals (20), or even better on a rubber pad (49), or simply by swinging it in a circular plane (48), or moving it like a pendulum at an amplitude of the

oscillations of 15–20° from the vertical position (51). Hauser and Reed (49), using fine-particle-size fractions of bentonite, obtained by supercentrifuging bentonite sols, were the first to prove, contrary to previous statements (23), that such bentonite sols were not only thixotropic, but also pronouncedly rheopectic.

The difference in thixotropic and rheopectic setting time and the influence of particle size is shown in figure 20 (51). The same effect can be obtained by adding to the negatively charged hydrogen bentonite a positively charged colloid, as, for example, iron oxide. If one adds 0.025 g. of it to 1 g. of hydrogen bentonite (dry weights), a gel results which has a thixotropic setting time in excess of 130 hr., but only 2 min. of rheopectic setting time (51). In view of the presence of iron oxide in many clay deposits, this phenomenon deserves more attention than it has so far received, particularly in geology, petrography, and

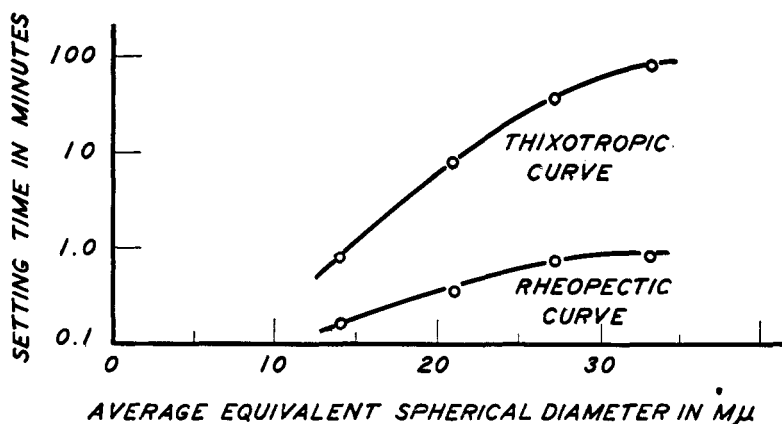


FIG. 20. Influence of particle size on setting time: 0.85 per cent bentonite; 76.5 millimoles potassium hydroxide per liter; temperature, 25°C. (51).

soil chemistry. The only other reference to rheopecty in clay systems is a statement by Freundlich (19) that the finest fractions of Solnhofen slate exhibit this phenomenon. This discovery deserves special attention, because it offers the most plausible explanation for the formation of the perfect petrifications of jellyfish for which these slates are well known. Similar findings in other parts of the world have always perplexed geologists (21).

Whereas thixotropic systems have been obtained from all possible types of colloidal dispersions, truly rheopectic systems seem to be limited to laminar systems, for which the clays are perfect examples. Besides this, rheopectic clay systems are limited to those clays which also permit production of thixotropic systems.

Whereas the setting up of a thixotropic gel does not call for any preferential alignment of the dispersed particles, ultramicroscopic studies of rheopectic systems indicate that the rhythmic motion applied to the sol orients and aligns

the platy particles and thereby accelerates their taking up the equilibrium positions already referred to when discussing the phenomenon of thixotropy.

Figure 21 represents a schematic interpretation of such alignment.

G. Stream double refraction

If one views a colloidal sol containing anisometric particles, preferably of rod or plate shape, between crossed Nicol prisms or crossed Polaroid sheets against a strong light source, no double refraction can be noticed. The reason for this is that the colloidal particles are subjected to constant Brownian molecular motion and are thereby prevented from taking up any preferential orientation. However, if such a sol is caused to flow, the disperse particles will always tend

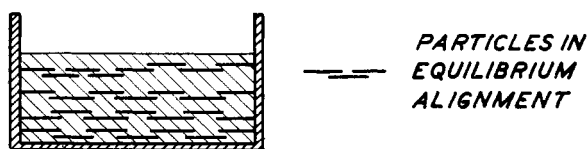


FIG. 21. Alignment of particles in a rheopectic system after setting caused by tapping container on flat table.

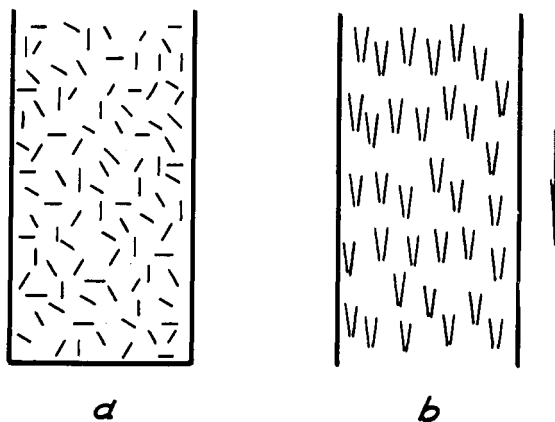


FIG. 22. (a) Complete disorder of platy colloidal particles dispersed in a stagnant liquid; (b) alignment of platy colloidal particles dispersed in a flowing liquid.

to orient in such a way that the planes of the disks or plates lie tangent to the surface of cones whose apexes point in the direction of flow (65, 70), and such a system will then exhibit the phenomenon known as stream double refraction or birefringence (figure 22).

Since most clays are composed of platy particles, it is only logical to assume that they must exhibit this phenomenon. This is actually the case, but permanent effects can only be expected if truly colloidal clays are used, because only then can one eliminate sedimentation of the disperse phase (3). Langmuir's (65) studies of polarization of light passing through a flowing bentonite sol indicate that the clay particles are thin flat plates of irregular shape, their lengths

being only somewhat greater than their widths. A purified, monodisperse bentonite sol of 1 per cent concentration, produced by supercentrifuging and containing particles ranging in apparent spherical diameter between 15 and 50 $m\mu$, proved particularly suitable (42) for studies of stream double refraction, because such a sol is quite clear to the eye, has practically the same viscosity and surface tension as water, and exhibits pronounced birefringence at extremely low rates of flow and for any temperature up to the boiling point of water (44).

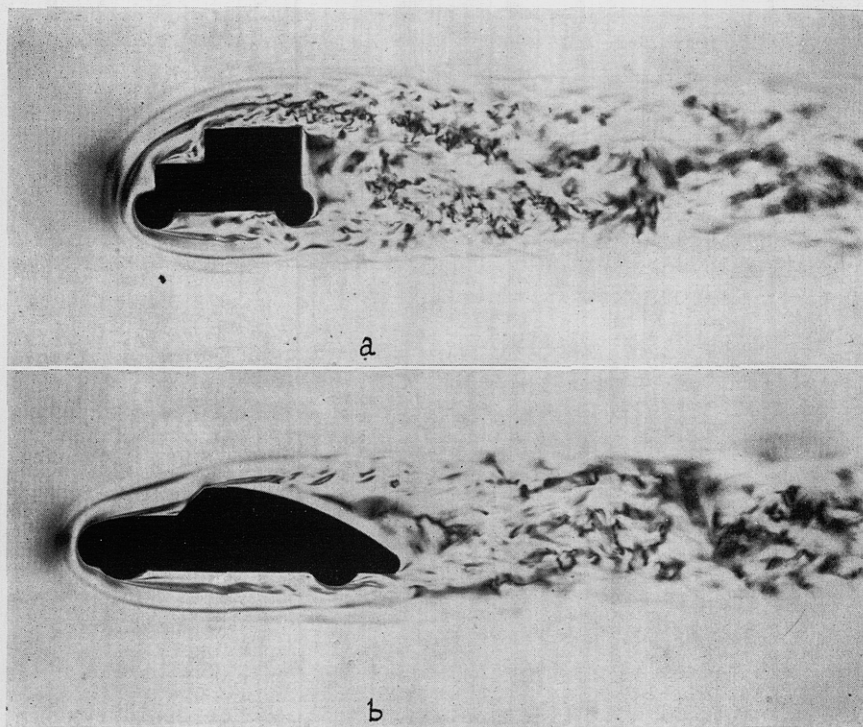


FIG. 23. Flow patterns, as shown with circular polarized light, around models depicting (a) the old-fashioned *versus* (b) the more modern streamlined body of an automobile traveling at high speed (45).

This property of colloidal clays has permitted the development of a very precise technique for studying flow patterns visually. Experimental measurements of the amount of double refraction caused by different values of velocity gradients enable one to interpret quantitatively the patterns in regions of laminar flow or even turbulent flow conditions. Figure 23 gives an idea of the applicability of this technique in engineering (45). War conditions do not permit as yet the discussion of further developments of this technique, made during the last few years in the fields of aeronautics and shipbuilding. However, the method has also been very successfully applied in the study of firebox design of railroad locomotives and other railroad engineering problems (66), and it is finding

increasing use in the visual study of the efficiency of water turbines, condenser scoops, and other hydraulic machinery (33).

Similar effects are obtained by applying an electric field to the system. This method permits optical study and measure of inhomogeneous electric fields in liquids comparable to studies of photoelasticity of solids (43, 76).

V. APPLIED COLLOID CHEMISTRY OF CLAYS

From the foregoing discussion of the most important colloidal phenomena and properties of clays, it must be evident that not only can their industrial use now be put on a far more intelligent basis,² but new applications have come and will keep on coming to light. In the following pages those fields of science and technology will be briefly discussed in which the colloid chemistry of clay minerals has already proved its value and which are considered to be most important. Many other uses, as for example in the production of emulsions, in the bonding of foundry sands, in insecticide and fungicide or bactericide sprays, and in lubricants, have not been specifically referred to, because the use of colloidal clays for these purposes must be self-evident when their colloidal properties and phenomena are taken into consideration.

A. *Ceramics* (30, 47, 78)

Of all the industries in which clay minerals are of predominant importance, the ceramic industry is, of course, the dominating one. It is the property of plasticity, so characteristic of clays, which permits their forming to practically any desired shape. However, not all clays exhibit this property to the same degree, and therefore pottery was for centuries an art which had to rely on trial and error tests before the suitability of a clay or mixtures of different clays could be established. With the comparatively recent development of the concept of the clay particle as a colloidal micelle it has not only been possible to offer a better understanding of such properties as plasticity, dry strength, shrinkage, and others, but it has also been clearly shown that the change of ceramics from an art to a science was at hand. By applying the new concept and its many ramifications intelligently, this change has been accomplished comparatively recently. Not only have we now a clear picture of the phenomena so important in ceramics but, knowing the reasons for their occurrence, we have also learned to control them, to change them when needed, and to apply them in such a way and to just such a degree as is most profitable for the purpose. As can be readily seen from the foregoing discussions, ceramics depends on modern colloid chemistry far more than is generally assumed, and recent developments in this field of applied colloid chemistry have offered the best proof for this point of view.

B. *Agriculture* (61)

Since clay is one of the fundamentally most important substances in soils, it is understandable that more attention is now being paid to clay research in

² C. G. Harman and C. W. Parmelee have just published a paper, "Fundamental Properties of Raw Clays Influencing their Use" (J. Am. Ceram. Soc. **28**, 110 (1945)), which offers further proof for the importance of surface or colloidal phenomena in clay-water systems.

connection with agriculture than ever before. The clay content and the type of clay present in the soil control above all its moisture content, its ability to supply water, its acidity, its tilth, and its general properties. Our increased knowledge of the colloid chemistry of clays and of its application in agriculture is already contributing its share for a deepening of our knowledge in the domain of soil science.

C. Soil engineering

The ion-exchange reaction of clay minerals has also become of importance in the domain of construction engineering. The application of this colloidal phenomenon for reduction of soil permeability or seepage is so far the most striking evidence for the value these new concepts have in fields where the application of chemistry was unknown only a short time ago.

Take, for example, the fresh-water lake on Treasure Island in San Francisco Bay. When built, the seven-acre lagoon showed a drop of 1 in. per day of its water level, which made it questionable if the lagoon could be maintained. The answer was simple. The sea water from the bay was pumped in and the pervious natural soil was transformed by ion adsorption and exchange into a non-pervious sodium soil. The sea water was removed and the lagoon filled with fresh water. The loss in level due to seepage dropped to 0.1 in. or even less per day (67).

The importance of a combination of our knowledge of the structure, chemical composition, and colloid-chemical considerations of clays has also proved its value in soil stabilization. This is of particular importance in highway engineering, construction of dams, and flood control (101).

D. Drilling muds

As has already been pointed out, montmorillonite, the major component of bentonite, exhibits the phenomenon of thixotropy to a very pronounced degree. It is this property which makes suspensions of this type of clay so well suited to the use to which so-called drilling muds are being put. The purpose of the mud is to hold the rock fragments obtained during the drilling of an oil well in suspension if the drill is at rest so that they do not sediment and form a cake around the drill and shaft. However, when the drill works it should find a minimum of resistance, and the liquid carrying the rock fragments or sand should have a low viscosity, so that it can be easily removed from the bore hold by pumping. A dispersion of clay whose repulsive and attractive forces have been so adjusted that a thixotropic system is created fulfills these requirements (43). Such drilling muds are also used to seal off formations traversed during the drilling operations, so that liquids or gases contained therein cannot interfere with the drilling operation or with the use of the oil well when put into operation (43).

E. Films and plastics

One of the most interesting and recent discoveries in the field of applied colloid chemistry of clays is their use in the production of coherent, self-supporting, and flexible films and their applicability as the basic material for mold-

able plastics (14, 41, 43, 94, 96). These films have been termed "Alsifilm" (*aluminum silicate films*).

If a thixotropic gel of grit-free montmorillonite, preferably one exhibiting high base-exchange capacity, is spread onto a smooth surface and subjected to careful drying, a film will form which, being coherent and self-supporting, can be easily removed from its support. By using conventional-type spreading machines, the process can be made continuous and the formed film wound up on a mandrel just as in the production of paper or other organic film or sheet-forming substances. If one observes the transition from the gel state to the coherent dry film with the use of an ultramicroscope of the Ultropak type (38), one can see how the clay ultramicros align themselves during evaporation and form intersecting and interweaving threadlike aggregates until a micro-fabric

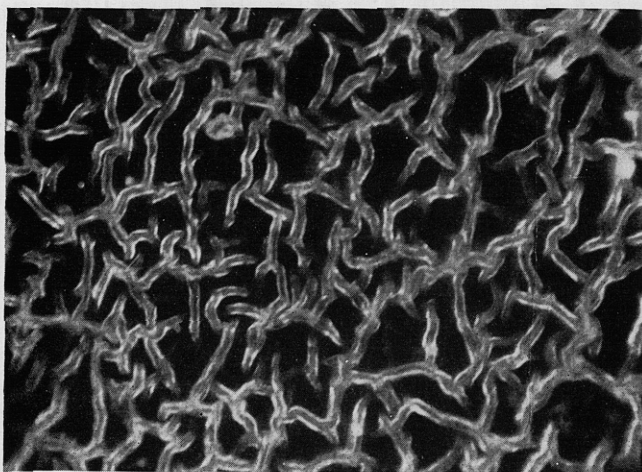


FIG. 24. Ultropak microphotograph of the structure of a crude montmorillonite film (Alsifilm) after being heated to 250°C. (42).

structure, as shown in figure 24, results. X-ray diagrams of such films taken parallel and at a right angle to their plane yield a typical Debye-Scherrer diffraction pattern of the clay mineral in the latter case, but a fibre pattern in the former. This proves that all the particles have aligned with the same crystallographic axis parallel to the support (42).

These films still exhibit all the properties of the original clay. In contact with water they will eventually again revert to a sol. Marshall and his coworkers have shown that such sheets made from the clay minerals montmorillonite or beidellite are of great value when used as membrane electrodes in the study of cation activities with a precision within 5 per cent at pH values above 4 (71, 72, 75).

The fact that the crude clay film is not resistant to humid atmospheres or moisture, even if compounded with water-resistant fillers or fibres like paper pulp (41), drastically limited its use. However, the fact that Alsifilm still permits base exchange has made it possible to transform the swellable and

redispersible film into an absolutely non-swellable condition by binding the ultimate clay particles to each other by the use of the proper type of ions (41, 42, 53).

The result is a film which is no longer affected by moisture. Its structure is comparable to that of muscovite and might, for reasons schematically shown in figure 25, be called synthetic mica (103).

Of particular interest is the fact that base exchange can also be accomplished with ions carrying organic radicals, as, for example, organic ammonium complexes which, after drying, can be condensed or even polymerized. Thus we have before us an interesting link between the inorganic and organic worlds.

Clay films which have been rendered water insoluble are excellent electric insulators, approaching the best types of mica in this respect. They are oil resistant and are not affected by organic solvents, fats, and waxes, and should, therefore, find interesting application in the field of packaging.

If paper is coated with such coherent clay films, its surface will become glossy and very resistant to all kinds of destructive influences.

The same inertness is also one of the outstanding characteristics of molded goods made from clays which have been base exchanged as described. By using appropriate organic exchange ions, another interesting link between ceramics and plastics has been established.

F. Thixotropic rubber compounds

The viscosity of the natural milk sap or latex of the rubber tree is very low if one compares it with the viscosity of a solution of rubber in an organic solvent, even if the concentration of rubber is many times that of the organic solution. Although this low viscosity has many advantages for the use of latex, it is a serious drawback wherever too great a fluidity of the system is disadvantageous. It is much easier to squirt a latex compound through a fine nozzle than a highly viscous solution of rubber in benzene, and the concentration in rubber will be much greater for any given volume. But, owing to its low viscosity, the latex would tend to spread out when deposited on a surface, as in the ends of container closures and the like. However, if a thixotropy-inducing clay dispersion is added to the latex, the compound will set up to a gel as soon as the dispersion has come to rest, and spreading will be avoided. This has made it possible to produce latex compounds which can be easily applied to the groove in a can end. The thixotropy of the compound will cause it to set up as soon as it comes to rest in the can end. It is then dried and the resulting rubber ring used as the seal for the food container (9).

G. Thixotropic adhesives

In the production of adhesive pastes containing rubber as the constituent causing adhesion, as used in the shoe industry, it is advantageous to have a paste which can be easily applied by brushing but which, as soon as applied, will set and thereby avoid flow or uneven distribution. Here again the application of thixotropy has proved of extreme value. Such adhesives (8) are composed of rubber latex to which a bentonite dispersion has been added.

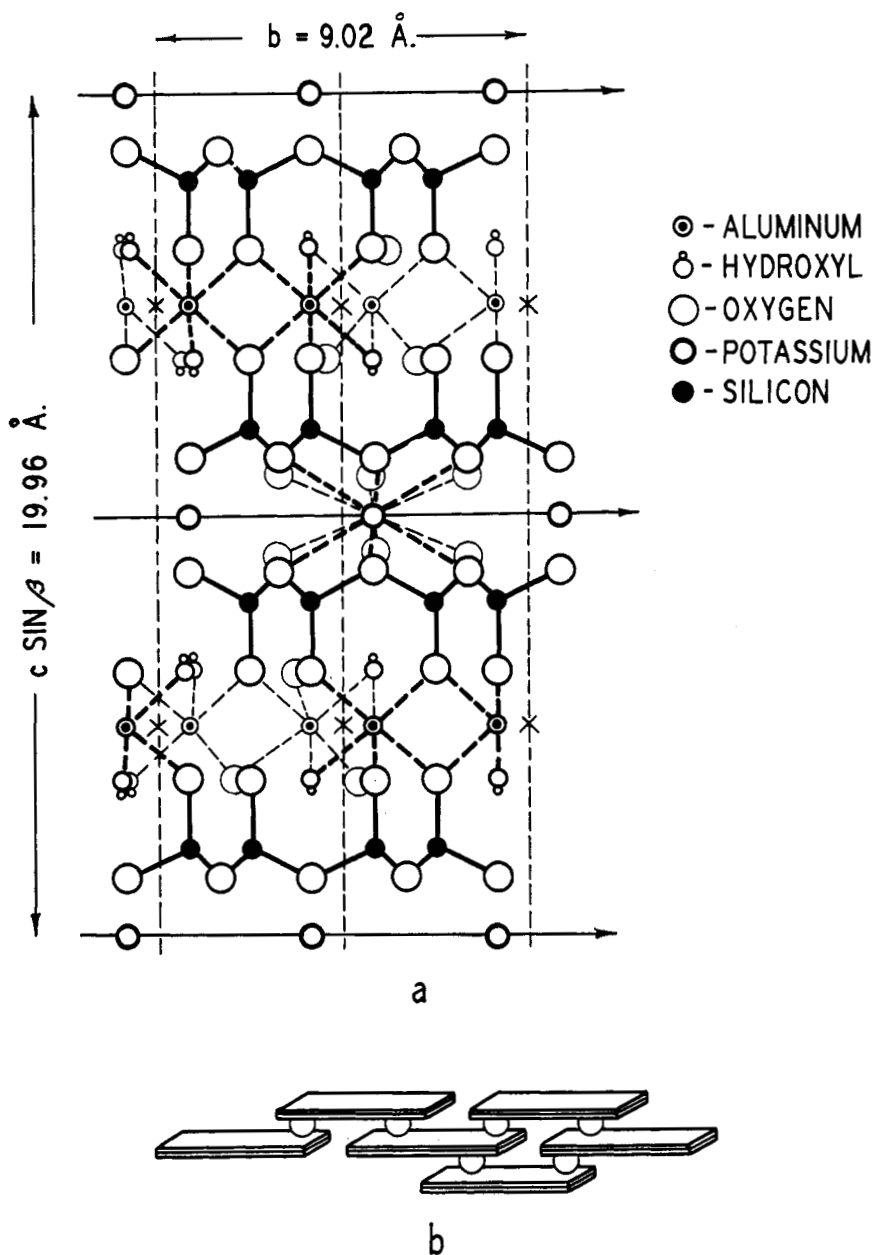


FIG. 25 (reference 42). (a) Schematic drawing of the structure of mica (muscovite) projected at a plane normal to the a -axis. The double sheets are seen with potassium atoms between them surrounded by twelve oxygen atoms (from W. L. Bragg: *Atomic Structure of Minerals*, p. 207, Cornell University Press, Ithaca, New York (1937)).

(b) Probable bonding of unit layer parcels of montmorillonite by large cations, producing water-resistant clay films.

This adhesive, therefore, when brushed onto the leather will flow readily, but as soon as the brushing is stopped it will, owing to the thixotropy of the bentonite, set and form a stable adhesive layer.

H. Water softening (97)

A very important application of clays which possess the property of ion exchange is in water softening. If hard water, which contains calcium and magnesium salts, is percolated through a bed filled with clay which carries sodium ions as its exchangeable counter ions, they will, as was shown in figure 15, be replaced by the calcium or magnesium ions until all the accessible free negative valencies of the clay particles are compensated by the concentration and valency of the added cations. Then, by applying the mass-action law, i.e., by using a high concentration of a concentrated solution of a sodium salt, like brine, one can regenerate the clay and again form a sodium clay.

Another technical application of the ion-exchange reaction can be found in the production of hydrocyanic acid from formamide, where natural aluminosilicates are used as dehydrating agents (56). Their application as nuclei for catalysts, by introducing appropriate metallic ions, has also been suggested (88).

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³ *Note added in proof:* Since this article was submitted for publication a few papers have appeared which should be mentioned to keep this review up to date.

C. C. Ross has published a paper entitled "Minerals and Mineral Relationships of the Clay Minerals" (*J. Am. Ceram. Soc.* **28**, 173 (1945)), in which he discusses in great detail the properties of colloidal clays and the possibilities of applying base-exchange reactions for specific purposes.

S. Sussman and A. B. Mindler have published a paper entitled "Ion Exchange—An Old Process Finds New Uses" (*Chem. Industries* **56**, 789 (1945)), in which a number of new applications for ion-exchange materials are discussed.

S. B. Hendricks has published a paper entitled "Base Exchange of Crystalline Silicates" (*Ind. Eng. Chem.* **37**, 625 (1945)), in which crystallographic properties are correlated with the base-exchange capacity of the various clays.

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