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CLAY–POLYMER INTERACTIONS: SUMMARY AND PERSPECTIVES

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Abstract—The adsorption of uncharged polymers by clays is largely "entropy-driven." Polymer conformation changes from a random coil in solution to an extended form at the surface in which adsorbed polymer segments or trains alternate with loops and tails extending away from the surface. Although the net interaction energy, ϵ, per segment-surface contact is small (~1 kT unit), the total energy of adsorption is large because the fraction of train segments, p, is commonly between 0.3 and 0.5. The adsorption isotherms are typically of the high-affinity type, and there is an apparent lack of desorption on dilution. Positively charged polymers (polycations) are adsorbed largely through electrostatic interactions between the cationic groups of the polymer and the negatively charged sites at the clay surface. Here $\epsilon \gg 1$ kT unit and $p > 0.7$, leading to an almost complete collapse of the polymer chain onto the surface. Indeed, beyond a given level of adsorption charge reversal can occur in that the clay–polycation system effectively behaves as an anion exchanger. Little adsorption occurs with negatively charged polymers (polyanions) due to initial charge repulsion between the polymer and the clay surface. Acid pH, a high ionic strength, and the presence of polyvalent cations in the system enhance and promote polyanion adsorption. Uncharged polymers and polycations can enter the interlayer space of expanding 2:1 type layer silicates but polyanions generally fail to intercalate.

The interactions of clays with biopolymers, such as proteins, nucleic acids, and polysaccharides, can be rationalized in similar terms. When intercalation occurs, the interlayer biopolymer is further stabilized against microbial (enzymatic) degradation giving rise to practical applications of clay–polymer complexes as flocculants and soil conditioners. Polyanions are effective as flocculants because of their large "grappling distance," whereas uncharged polymers are better suited as soil conditioners because they can spread over adjacent clay/soil particle surfaces like a coat of paint.

Key Words—Adsorption, Anion exchange, Flocculants, Montmorillonite, Polyanion, Polymer, Soil conditioner.

INTRODUCTION

The interactions of clays with organic polymers have attracted the interest of soil scientists for a long time (Schloesing, 1874), being prompted by the biostability of soil organic matter ("humus") which, for the most part, is a mixture of dark-colored polyanions, referred to as humic substances. It is now generally accepted that clay–humus interaction in soil plays an important and sometimes crucial role in many soil processes, such as mineral cycling and weathering, profile development, and aggregate stabilization. Indeed, the oft-quoted statement by Jacks (1963) that this interaction is ". . . as vital to the continuance of life as, and less understood than, photosynthesis" is not as farfetched as it might sound. With the possible exception of some desert and polar soils, surface soils are essentially clay- or mineral-organic complex systems.

Since the early 1940's rapid advances have been made in our understanding of the principles underlying the interactions of clays with organic compounds. For many systems involving small organic molecules, fairly accurate predictions can be made about the mode of bonding and the orientation of the adsorbed species at the clay surface (Mortland, 1970; Theng, 1974). Although the information gained from adsorption studies of short-chain organic species forms the basis for interpreting the behavior of polymeric compounds at clay mineral surfaces, additional variables enter the picture when dealing with organic macromolecules. Besides being long, polymer chains are flexible, multisegmented, and polyfunctional. They may, therefore, adopt various conformations in solution and become attached to the clay surface by numerous segment–surface bonds. In addition, accessibility, solubility, and steric factors come into play during the interaction process. Even the order and way in which the components of the system are brought together and mixed can influence the resultant complexes. For these reasons, clay-polymer chemistry is still largely a descriptive science, and the clay–polymer interaction can at best be discussed in semiquantitative terms (Theng, 1979).

The following review highlights the interactions of layer silicate minerals with selected polymers of the charged and uncharged type in an aqueous environment.

ASPECTS OF POLYMER ADSORPTION

The adsorption of an uncharged, flexible, linear polymer onto a clay surface generally leads to the desorption of numerous solvent (here water) molecules from

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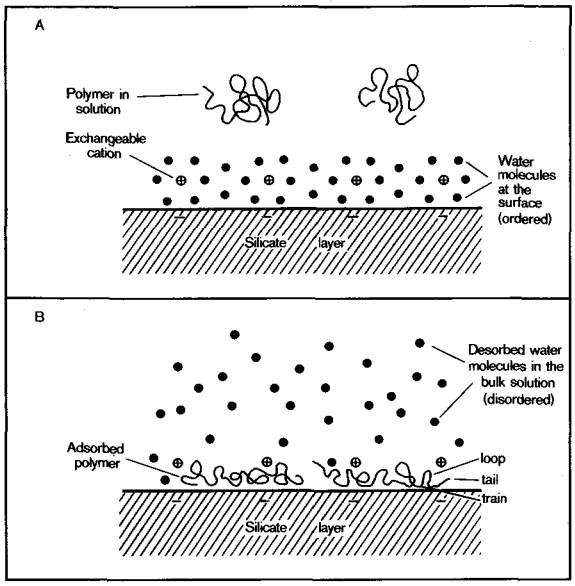


Figure 1. Diagram illustrating the desorption of numerous water molecules from a clay surface during the adsorption of an uncharged linear polymer, leading to a net gain in entropy by the system. The change in polymer conformation from a random coil in solution to a more or less extended one at the clay/solution interface is also indicated.

the surface. The entropy so gained provides the driving force for adsorption because the enthalpy change of the process is commonly very small and may even be positive. Thus, the adsorption of polymers, especially of high molecular weight species, is largely an "entropy-driven" process. The data of Parfitt and Greenland (1970a) for polyethylene glycols adsorbing onto Ca-montmorillonite illustrate these points (Table 1).

Adsorption also leads to a change in conformation in that the polymer, which in solution tends to exist as a random coil, uncoils and spreads out at the solid/solution interface. Thus, the surface conformation is one in which contiguous sequences of adsorbed segments or "trains" alternate with three-dimensional "loops" extending away from the surface, and the polymer chain terminates in two free-dangling "tails" (Figure 1). Even when the net segment-surface interaction energy, ϵ, is only of the order of 1 kT unit, the total energy of adsorption can be very large because there are so many adsorbed segments. The fraction of train segments, p, is therefore an important parameter which for uncharged polymers is commonly between 0.3 and 0.5, i.e., an average of 40% of the total number of segments in the polymer chain can be attached to the mineral surface.

The strong interaction of uncharged polymers with clays means that a great deal of material can be removed even from dilute (<0.2% w/v) solutions so that

Table 1. Data for the interlayer adsorption of polyethylene glycols (PEG) and associated change in entropy (ΔS).[1]

Molecular weight of PEG	Weight of PEG adsorbed (g/100 g)	Volume of PEG adsorbed[2] (cm^3/g)	Volume of water desorbed (cm^3/g)	ΔS (entropy units)
200	7.0[3]	0.070	0.110	−0.2
300	13.5[3]	0.114	0.114	+2.0
400	14.6[3]	0.124	0.124	+2.8
600	19.0[4]	0.160	0.132	+11.1

[1] From Parfitt and Greenland (1970a).
[2] Taking 61×10^{-24} cm^3 as the volume per segment (monomer unit).
[3] At the upper limit of isotherm linearity.
[4] At plateau adsorption.

the isotherms for polymer adsorption are commonly of the "high-affinity" (H) type (cf. Figure 8). Indeed, the most informative region of the isotherm corresponding to the initial rapid rise may be experimentally inaccessible because its slope is so steep. By the same token, the rate of polymer desorption in the same solvent system is very small; so much so, that adsorption is commonly virtually "irreversible" because of the small probability that all train segments can be simultaneously detached from the surface and remain so sufficiently long for the polymer chain to move away from the interface into the bulk solution. Recent theoretical analyses by Cohen Stuart *et al.* (1980), however, suggest that the apparent lack of desorption on dilution can, in many cases, be ascribed to polydispersity.

As might be expected, the amount adsorbed increases with the size or molecular weight of the polymer, if surface accessibility is not restricted, e.g., in dilute suspensions of Na-montmorillonite. However, the opposite behavior, that is, one in which uptake decreases as molecular weight increases, is by no means uncommon, and is illustrated by condensed clay-water systems (e.g., illite, kaolinite, and montmorillonite saturated with cations other than Na or Li). Such systems are essentially "porous," and molecules beyond a certain size are physically excluded from some pore surfaces. Figure 2 illustrates these points.

The interactions of charged polymers with clays are, if anything, more complex than those involving nonionic species (Hesselink, 1977). Apart from the variables mentioned above, polyelectrolytes can undergo changes in surface charge and conformation (stretching-coiling transformations) in response to changes in the pH and ionic strength of the ambient solution. These effects are of great importance in the use of polyelectrolytes as aggregating/flocculating agents of clay and colloidal dispersions.

The adsorption of positively charged polymers or polycations by clays largely occurs through electrostatic (coulombic) interactions between the cationic groups on the polymer and the negatively charged sites

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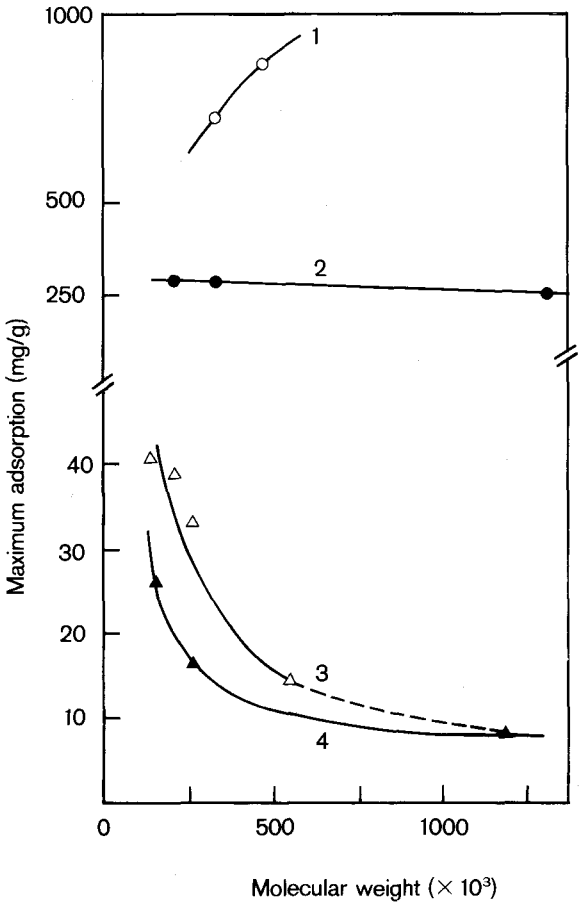


Figure 2. Influence of molecular weight on the adsorption of uncharged polyacrylamide from aqueous solutions at 25°C by different clay minerals. Curve 1, Na-montmorillonite; curve 2, H/Al-montmorillonite; curve 3, H/Al-illite; curve 4, H/Al-kaolinite (after Schamp and Huylebroeck, 1973).

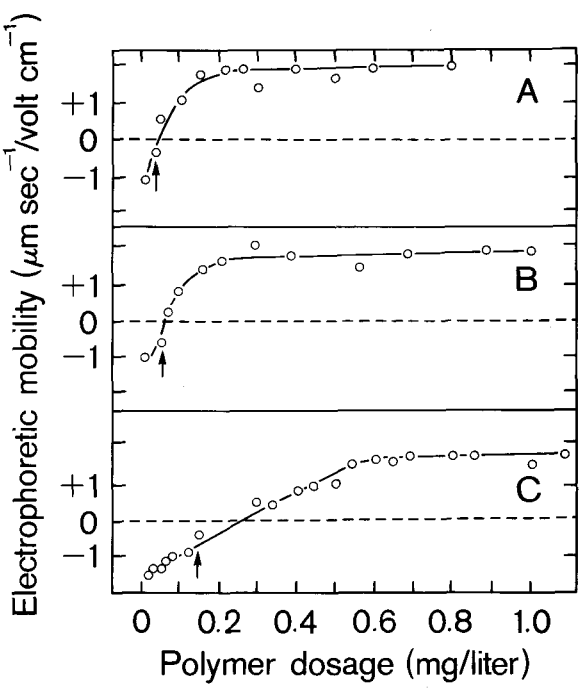


Figure 3. Changes in electrophoretic mobility of kaolinite suspensions on adding a polycation (N-substituted piperidinium chloride polymer). Initial clay concentration: 14.9 mg/liter (A), 29.8 mg/liter (B), 73.2 mg/liter (C). Note the charge reversal as the polymer dosage is increased beyond a certain level. Arrows indicate the concentration of polycation at which maximum aggregation (coagulation) occurred (after Black *et al.*, 1966).

at the mineral surface. Indeed, beyond a given level of uptake a reversal of "surface" charge (from negative to positive) takes place, as shown in Figure 3. Here, the value of ϵ greatly exceeds 1 kT unit, and adsorption generally leads to a rapid two-dimensional collapse of the polycation chain onto the surface with relatively few short loops ($p > 0.7$).

On the other hand, negatively charged polymers or polyanions tend to be repelled from the clay surface, and little adsorption occurs. Appreciable uptake, however, can take place under acid conditions and/or at high ionic strength when the negative charge on the polyanion becomes effectively neutralized by protonation and/or is screened by the electrolyte. Adsorption is also promoted by the presence of polyvalent cations which act as "bridges" between the anionic groups on the polymer and the negatively charged sites on the clay, as illustrated by the work of Mortensen (1962) (Figure 4). At acid pH, polyanions also adsorb onto the clay crystal edges by electrostatic interactions ("anion exchange") because aluminum exposed at these sites acquires a positive charge. Another possible bonding mode is that of "ligand exchange" by which the anionic group of the polymer enters the inner coordination layer of edge aluminum to form a coordination complex with it (Tate and Theng, 1980). On the whole, however, polyanions are adsorbed by relatively few train segments unless the system is allowed to dehydrate when other bonding modes of short-range order (e.g., van der Waals interactions) become operative. Another feature of their adsorption is that, unlike uncharged and positively charged polymers, polyanions do not enter the interlayer space of expanding layer silicates (e.g., Ruehrwein and Ward, 1952). However, appreciable intercalation may occur at low pH when the polyanion behaves and adsorbs like an uncharged species (Schnitzer and Kodama, 1966).

FORMATION AND PROPERTIES OF CLAY-POLYMER COMPLEXES

By way of illustrating the above principles experimental data on the clay–polymer interaction may be cited, taking polyvinyl alcohol (PVA), cationic poly-

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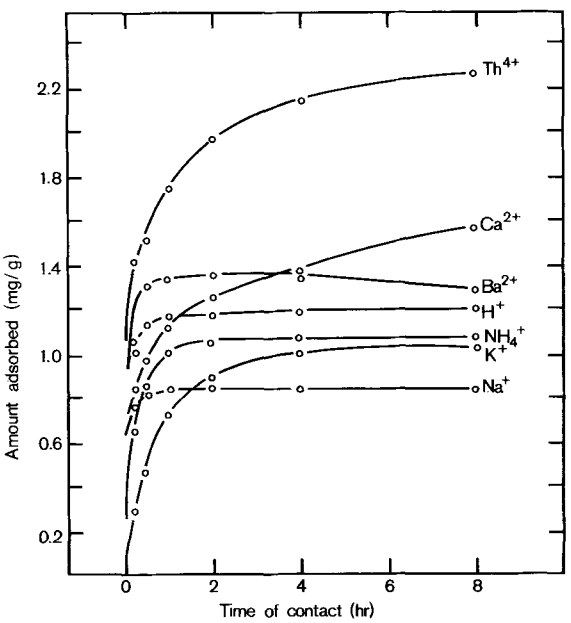


Figure 4. Adsorption of hydrolyzed polyacrylonitrile (a polyanion) from aqueous solutions by kaolinite as influenced by the nature of the exchangeable cation at the clay surface (after Mortensen, 1962).

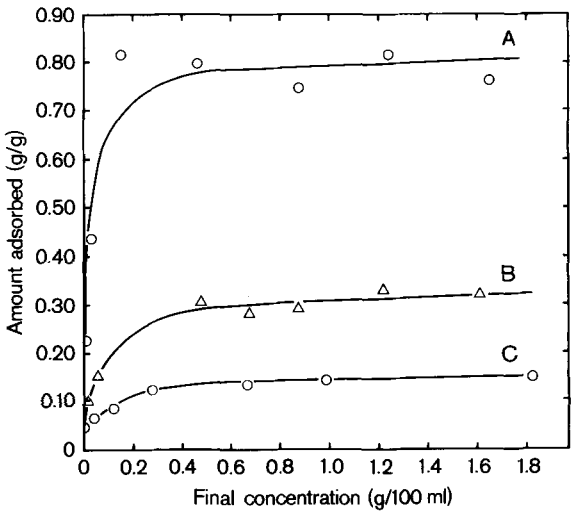


Figure 5. Adsorption of polyvinyl alcohol (molecular weight 25×10^3) from aqueous solutions by montmorillonite. The polymer solution was added to air-dry clay to give a 0.5% w/v suspension. A = Na-montmorillonite; B = Ca-montmorillonite; C = Cs-montmorillonite (after Greenland, 1963).

sulfone, and soil fulvic acid as examples of an uncharged polymer, a polycation, and a polyanion, respectively. The adsorption of PVA by montmorillonite is influenced by the nature of the exchangeable cation and by ionic strength (Greenland, 1963), as shown in Figure 5. These results may be rationalized in the following way. In water (zero ionic strength), Na-montmorillonite crystals swell and give basal spacings of ~130 Å, whereas the Ca- and Cs-forms do not expand beyond a d(001) value of ~19 and ~15 Å, respectively. The coil dimensions of PVA (molecular weight range, 17,000–67,000) in solution are 44–67.5 Å and 53–117 Å for the hydrodynamic and root mean square radii, respectively (Garvey *et al.*, 1976). Thus, the polymer can presumably gain unrestricted entry into all external and internal crystal surfaces of Na-montmorillonite, giving rise to a relatively large uptake (cf. Figure 2). By the same token, interlayer entry is severely restricted for the Ca-clay and impossible for the Cs-clay. The amount adsorbed is correspondingly reduced as compared with the Na-clay. The addition of electrolytes, such as $NaNO_3$, to the Na-clay suspension reduces interlayer swelling. Accessibility of interlayer surfaces to the polymer is thereby reduced, and uptake falls off accordingly (Figure 6).

The complex with Na-montmorillonite at maximum adsorption of PVA (~0.8 g/g) has a basal spacing of ~30 Å, corresponding to an interlayer separation of ~20 Å (Figure 5). For an interlayer area of ~750 m^2/g, the maximum amount adsorbed is compatible with a rather

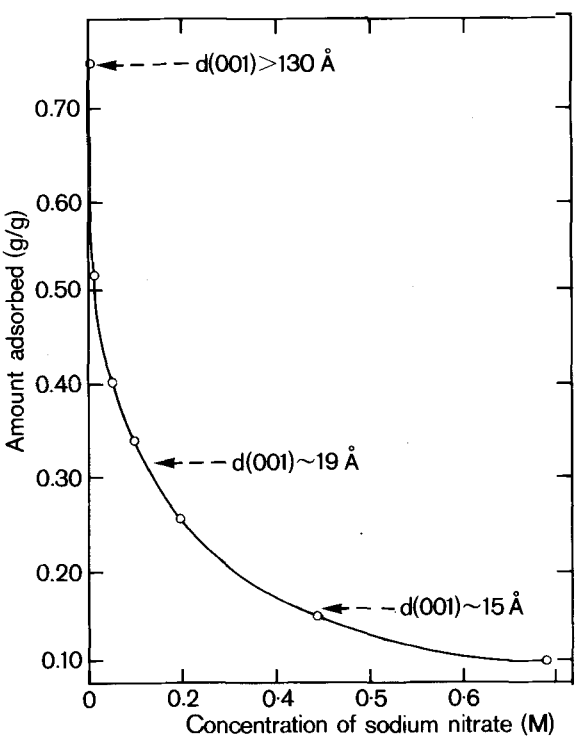


Figure 6. Effect of ionic strength on the adsorption of polyvinyl alcohol by Na-montmorillonite. The basal spacing of ~130 Å for the Na-clay in distilled water can be reduced to the level of its Ca (~19 Å) and Cs (~15 Å) forms by electrolyte (here $NaNO_3$) addition. The polymer was added to 6% w/v aqueous suspensions of clay to form 1% w/v final suspensions (after Greenland, 1963).

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Table 2. Adsorption of a cationic polysulfone[1] by montmorillonite.[2]

(A) Amount adsorbed (meq/100 g)	(B) CEC (meq/100 g)	(C) AEC (meq/100 g)	(D) Amount in trains (meq/100 g) (Column A−Column C)	Sum of columns (B) + (D) (meq/100 g)	Proportion of segments in trains (p) Colume D/ Column A
0	62.4	0	0	62.4	1
8.56	49.6	0	8.56	58.1	1
18.5	44.6	0	18.5	63.1	1
33.6	30.7	0.97	32.6	63.3	0.97
40.7	24.5	3.85	36.8	61.3	0.90
43.5	23.9	5.34	38.2	62.1	0.88
47.9	21.4	6.68	41.2	62.6	0.86
46.6	23.7	6.37	40.2	63.9	0.86
57.7	15.8	13.2	44.5	60.3	0.77
58.5	14.4	15.1	43.4	57.8	0.74
63.0	12.8	15.5	47.5	60.3	0.75
64.3	11.1	18.2	46.1	57.2	0.71

[1] Diallyldimethylammonium chloride-SO_2 copolymer; molecular weight 16.7×10^4.
[2] Suspension concentration = 1.5 g/100 ml; 30°C.
[3] From Ueda and Harada (1968).

flat, extended monolayer of PVA on each of two opposing interlayer surfaces, with an average loop length of 10 Å and a p-value of ~0.5.

That polycations are largely adsorbed by electrostatic interactions with the negatively charged sites at the clay surface, resulting in mutual charge neutralization and chain collapse, is demonstrated by the work of Ueda and Harada (1968). Using Na-montmorillonite with a cation-exchange capacity (CEC) of 62.4 meq/100 g, they followed the changes in CEC and anion-exchange capacity (AEC) of the complex with cationic polysulfone with progressive adsorption. Note in Table 2 that as the amount adsorbed increases, the AEC rises whilst the CEC declines. As the parent clay has no measurable AEC, the development of an AEC, i.e., of positive charges, by the complex can be ascribed to cationic groups contained in the loops and tails of the adsorbed polymer. By the same token, the decrease in CEC must be due to neutralization of the negative surface charges by train segments. The difference between the total amount adsorbed and the AEC therefore represents the amount of segments in trains. Interestingly, up to a surface coverage of ~0.5, all or nearly all of the polymer segments are adsorbed in the form of trains ($p \sim 1$); even at full coverage, only about 25% of the segments are contained in loops and tails.

The isotherms for the adsorption of a polyanion, such as fulvic acid (FA) by montmorillonite saturated with different polyvalent cations at pH 7, is shown in Figure 7 (Theng, 1976). The data are consistent with a cation-bridge type of interaction in that the affinity of FA for the clay surface is closely related to the ionic potential of the respective cation. The linearity of the isotherms indicates that fresh sites are created as adsorption progresses. Since there is no interlayer uptake, these sites are presumably located between clay crystals within a "domain" or in the "pores" between individual clay domains. However, if the solution pH is taken below 4, the ionization of the carboxyl groups on FA is suppressed, intercalation is possible, and adsorption is greatly increased (Schnitzer and Kodama, 1966).

The above considerations apply to the interactions of clays with biopolymers. Thus, the adsorption of proteins is pH-dependent, generally reaching a maximum close to the isoelectric point of the protein (McLaren *et al.*, 1958) (Figure 8). At this point the material is least soluble and so tends to accumulate at the clay/solution interface. Proteins, at least the globular type, apparently retain their gross native conformation on adsorption (Morrissey and Stromberg, 1974). The adsorption of enzymes by clays commonly leads to a reduction in their respective activity, and the pH-optimum for activity is shifted to more alkaline values (Ramirez-Martinez and McLaren, 1966). The presence of clays also modifies the maximum velocity and the Michaelis-Menten rate constant of the enzyme-catalyzed reaction (Kobayashi and Aomine, 1967; Makboul and Ottow, 1979). Complex formation between clays and proteins, especially when intercalation occurs, tends to "protect" the adsorbed species from enzymic attack (Estermann *et al.*, 1959).

As might be expected, the adsorption of nucleic acids and nucleoproteins by clays is sensitive to solution pH, generally decreasing with an increase in pH (Greaves and Wilson, 1969). Like most proteins, nucleic acids can intercalate into montmorillonite without undergoing a great deal of conformational change and so become stabilized against microbial decomposition. The strong adsorption of viruses by clays and soils is actually an advantage in that little virus gets into the ground-water system (Malina and Sagik, 1974).

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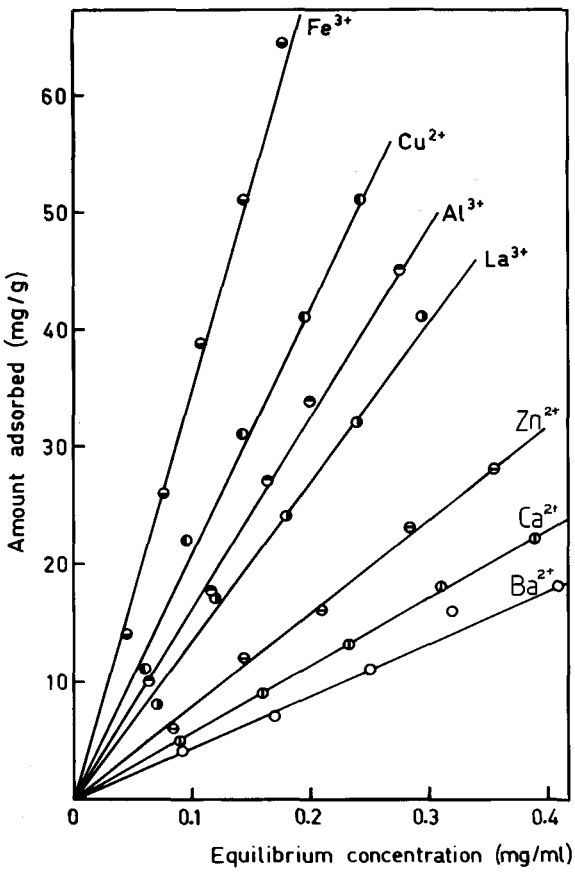


Figure 7. Isotherms for the adsorption at 20°C and pH 7 of fulvic acid by montmorillonite saturated with different cations. The slope of the isotherms, a measure of the affinity of the polymer for the surface, is related to the valency/radius ratio (i.e., ionic potential) of the respective cation (after Theng, 1976).

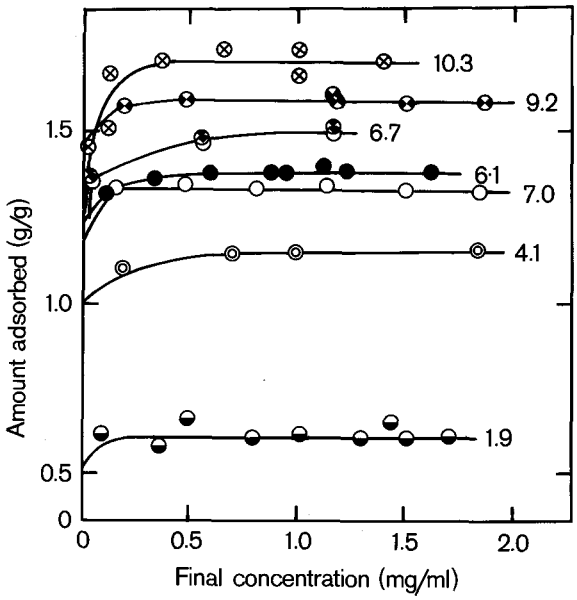


Figure 8. Isotherms for the adsorption at 25°C of lysozyme by montmorillonite at different solution pH values, ranging from 1.9 to 10.3. Highest uptake occurs at pH 10.3 close to the isoelectric point of lysozyme (after McLaren *et al.*, 1958).

Polysaccharides, important components of soil organic matter, may be uncharged, positively, or negatively charged; their interactions with clays vary accordingly. Thus, high-affinity type isotherms are obtained for the adsorption of uncharged polysaccharides (e.g., dextrans) by montmorillonite; the polymers are intercalated with a large fraction of their segments in trains (Olness and Clapp, 1975). Despite their relatively low intrinsic viscosity (molecular weight), positively charged polysaccharides (e.g., chitosan, deacetylated chitin) are adsorbed to the same extent as the most strongly adsorbed uncharged species (Clapp and Emerson, 1972). The former are presumably adsorbed with a larger segment-surface interaction energy as compared with the uncharged polymers of similar molecular weight, giving rise to a virtually complete collapse of the polycation onto the clay surface. By the same token, negatively charged polysaccharides (e.g., polygalacturonic acid) are apparently adsorbed by relatively few segments and the amount adsorbed depends on the nature of the exchangeable cations at the clay surface and the pH of the system (Parfitt and Greenland, 1970b). The adsorption of polysaccharides by clays and soils has received much attention because soil polysaccharides of bacterial origin are strongly implicated in soil aggregate stabilization (Hepper, 1975). Thus, the addition of polysaccharides to soil can markedly increase the amount and size of water-stable aggregates, and the polysaccharide content of many soils is positively correlated with the degree of aggregation. Polysaccharides are likely to be very important in soils whose total organic matter content is naturally low or has been depleted by cultivation.

PRACTICAL APPLICATIONS

The clay-polymer interaction has found many and varied practical applications in agriculture and chemical technology. One is the use of polymers as flocculants of dilute clay and colloidal dispersions in which the particles are separated by relatively large distances. Flocculation involves both attachment of the polymer onto the particle surface and the bridging of several particles by the adsorbed molecule. Because uncharged polymers exist as randomly coiled units rather than as extended chains in solution, they are generally not very effective as flocculating agents (Vincent, 1974). Polycations, as has been shown above, can neutralize the charge on clay particles and so serve as effective coagulants (Black *et al.*, 1966; cf. Figure 3); however,

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because of their rapid collapse onto the clay surface, only limited interparticle bridging can be achieved. On the other hand, polyanions are effective flocculants, especially in the presence of polyvalent cations (Roberts *et al.*, 1974), because only a few segments of the polymer chain are involved in adsorption; the majority are present in the form of long loops and tails. Thus, polyanions have a relatively large "grappling distance" that facilitates the formation of interparticle bridges.

Polymers have also been used as "soil conditioners," that is, materials capable of increasing the mechanical strength and water stability of soil aggregates (De Boodt and Gabriels, 1976). In many cases, the incorporation of polymers into soils also has a favorable effect on seed germination, seedling emergence, and crop yield. These effects stem more from the improvement in the physical conditions of the treated soils than from the presence of (a small amount of) polymer as such. Uncharged PVA types have been found to be effective because they spread like a "coat of paint" over the surface of soil/clay particles which are already in close proximity to each other (Greenland, 1963). Their effectiveness can be greatly increased by introducing the polymer at strategic positions into pores of a certain size range (15–50 μm) (Quirk and Williams, 1974). As might be expected, the larger the molecule, the more effective it is in stabilizing soil aggregates. For the reasons stated above, polyelectrolytes are relatively ineffective as aggregate stabilizers.

Industrially, clays are used as fillers and reinforcers in polymer systems, such as elastomers, polyethylene, polyvinyl chloride, and other thermoplastics, and as coating agents for various types of paper. All things being equal, the efficiency of a filler in improving the physico-mechanical properties of a polymer system is primarily determined by the degree of its dispersion in the polymer matrix. Because clay surfaces are essentially hydrophilic, raw or untreated clay is not readily dispersible in, or rapidly wet by, the organic phase. To make the mineral and organic phases mutually compatible, it is often necessary to render the clay surface organophilic prior to blending or compounding the filler with the polymer. This can be done by attaching a suitable organic compound to the filler surface (Helmer *et al.*, 1976), by exchanging the inorganic cations with organic counterparts (Jordan, 1963; Nahin, 1963), or by treating the mineral with organosilanes (Libby *et al.*, 1967). The most effective ways of achieving compatibility are to graft a suitable polymer onto the filler surface (Kaas and Gardlund, 1976) and/or to encapsulate the mineral particles with a polymer layer (Hawthorne *et al.*, 1974).

OUTLOOK

It is clear that clays cannot be regarded as chemically inert materials or substrates. Indeed, clays are known to catalyze a variety of organic reactions including those which lead to polymer formation (Theng, 1974). Some of these reactions, if not unique to clay systems, give yields much in excess of those obtained in homogeneous solutions. Examples of such reactions are the formation from their respective precursors of unusually bonded metal-arene complexes and higher molecular weight species (Doner and Mortland, 1969; Tricker *et al.*, 1975; Mortland and Halloran, 1976; Stoessel *et al.*, 1977), of polypeptides (Paecht-Horowitz, 1978), of polynucleotides (Ibanez *et al.*, 1971), and of porphyrins (Cady and Pinnavaia, 1978). Equally relevant in this context is the ability of clays to transform and alter a variety of organic compounds through reactions which, in the absence of clays, would only proceed under extreme or special experimental conditions. Thus, clays can catalyze the oxidative degradation of amino acids and phenolic compounds (Thompson and Tsunashina, 1973); in the latter system the reaction can lead to the formation of humic substances (Wang *et al.*, 1980). Similarly, clays acting as strong Lewis and/or Brønsted acids, can transform purines and pyrimidines (van der Velden *et al.*, 1973), sterols (De Leeuw *et al.*, 1973; Sieskind *et al.*, 1979) and fatty acids (Almon and Johns, 1976) to yield products which occur or closely resemble those in sediments and crude oil. By the same token, clays catalyze the dimerization and isomerization of alkenes (Sohn and Ozaki, 1980). Clays are also implicated in chemical evolution (Lahav and Chang, 1976) and in the prebiotic synthesis of organic molecules (Fripiat and Poncelet, 1973). The earlier literature on this topic has been summarized by Theng (1974). Some more recent examples are the formation of amino acids from KCN and their intercalation by montmorillonite (Aragon de la Cruz and Viton Barbolla, 1979), and from CH_4–N_2 under conditions simulating those of the primitive earth (Shimoyama *et al.*, 1977). It is in this area of organic catalysis/synthesis, and related processes such as chemical evolution, petroleum genesis/recovery (Foscolos *et al.*, 1976; Czarnecka and Gillott, 1980), and in soil-organic matter transformation (Tate and Theng, 1980) that future research is likely to develop.

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Резюме—Движущей силой адсорбции незаряженных полимеров глинами является, главным образом, энтропия. Конформация полимера изменяется от случайной спирали в растворе до вытянутой формы на поверхности, в которой сегменты адсорбированных полимеров либо их последовательные ряды чередуются с изогнутостями и концевыми частями, простирающимися от поверхности. Хотя чистая энергия взаимодействия, ϵ, на контакт сегмент, поверхность небольшая ($\sim$1 кТ), общая энергия адсорбции большая вследствие того, что фракция серийных сегментов, p, обычно находится в пределах между 0,3 и 0,5. Адсорбционные изотермы обычно большого родства и имеется также кажущееся отсутствие десорбции при разбавлении. Положительно заряженные полимеры (поликатионы) адсорбируются, главным образом, посредством электростатических взаимодействий между катионными группами полимера и отрицательно заряженными местами на поверхности глины. При этом $\epsilon \gg 1$ кТ и $p > 0{,}7$, что приводит к почти полному разрушенню полимерных цепочек на поверхности. Действительно, вне данного уровна адсорбции может выступить перемена знака заряда с тем, что система глина—поликатион эффективно ведет себя как обменник анионов. Вследствие начального отталкивания заряда между полимером и поверхностью глины появляется небольшая адсорбция с отрицательно заряженными полимерами (полианионами). Кислотность pH, большая ионная сила и присутствие многовалентных катионов в системе благоприятствуют и ускоряют адсорбцию полианионов. Незаряженные полимеры и поликатионы могут входить в межслойные пространства расширяющихся слоевых силикатов типа 2:1, только полианиоиы, в основном, отказываются переслаиваться.

Взаимодействия глин с биополимерами, такими как белки, нуклеиновые кислоты и полисакариды могут быть рационализированы подобным образом. Когда появляется прослойка, промежуточный биополимер стабилизируется в дальнейшем от микробного (ензиматического) распада приводя к практическому применению глинополимерных комплексов в качестве флоккулянтов и кондиционеров почвы. Полианионы эффективны как флоккулянты из-за их большого ,,схватывающего расстояния", в то время как незаряженные полимеры лучше удовлетворяют требованиям в качестве кондиционеров почвы, так как они могут растекаться по прилегающих частицах глины/почвы подобно растеканию краски. [E.C.]

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Resümee—Die Adsorption von ungeladenen Polymeren durch Tone hängt hauptsächlich von der Entropie ab. Die Polymerkonformation ändert sich von einer Spirale in der Lösung zu einer gestreckten Form an der Oberfläche, an der adsorbierte Polymer-Segmente oder Züge mit Polymer-Schleifen und -Enden abwechseln, die von der Oberfläche wegstehen. Obwohl die Vernetzungsenergie, ϵ, pro Segmentoberflächenkontakt gering ist (~1 kT), ist die gesamte Adsorptionsenergie groß, da die Spaltung der Polymersegmente, p, meistens zwischen 0,3 und 0,5 ist. Die Adsorptionsisotherme sind typisch vom Hochaffinitätstyp, wobei auch bei der Verdünnung eine Desorption offensichtlich fehlt. Positiv geladene Polymere (Polykationen) werden hauptsächlich durch elektrostatische Wechselwirkungen zwischen den kationischen Gruppen des Polymers und den negativ geladenen Stellen auf der Tonoberfläche adsorbiert. Dabei ist $\epsilon \gg 1$ kT und $p > 0{,}7$, was zu einem nahezu vollständigen Zusammenbrechen der Polymerketten auf der Oberfläche führt. Tatsächlich kann über einem bestimmten Grad der Adsorption eine Ladungsumkehr auftreten, wobei das Ton-Polykation-System wie ein Anionenaustauscher wirkt. Eine geringe Adsorption tritt bei negativ geladenen Polymeren (Polyanionen) auf, die auf dem anfänglichen Ladungsabstoß zwischen dem Polymer und der Tonoberfläche beruht. Ein saurer pH, eine groß Ionenstärke und die Anwesentheit von polyvalenten Kationen im System erhöhen und fördern die Adsorption von Polyanionen. Ungeladene Polymere und Polykationen können in den Zwischenraum von quellfähigen 2:1 Schichtsilikaten gehen, Polyanionen können dagegen im allgemeinen nicht eingebaut werden.

Die Wechselwirkungen von Tonen mit Biopolymeren, wie Proteinen, Nukleinsäuren und Polysaccharide, können auf ähnlichem Weg verwirklicht werden. Wenn ein Einbau stattfindet, ist das Zwischenschichtpolymer gegen mikrobiologischen (enzymischen) Abbau geschützt. Dies führt dazu, daß man Ton-Polymerkomplexe als Flockungsmittel und Bodenstabilisierungsmittel verwenden kann. Polykationen wirken wegen ihres großen "grappling distance" als Flockungsmittel, während ungeladene Polymere besser als Bodenstabilisierungsmittel geeignet sind, da sie sich wie eine Farbhaut über aneinander grenzende Ton/Boden-Teilchen breiten können. [U.W.]

Résumé—L'adsorption de corps polymères sans charge par des argiles est pour la plupart "conduite par entropie." La conformation de corps polymères change d'une bobine au hasard en solution en une forme étendue à la surface dans laquelle des segments ou des trains de corps polymères adsorbés alternent avec des boucles et des queues s'éloignant de la surface. Malgré que l'énergie nette d'interaction, ϵ, par contact segment-surface, est petite (~1 kT) l'énergie totale d'adsorption est grande parce que la fraction des segments de train, p, est souvent entre 0,3 et 0,5. Les isothermes d'adsorption sont typiquement de la sorte à haute affinité et il y a un manque apparent de désorption lors de la dilution. Les corps polymères chargés positivement (polycations) sont pour la plupart adsorbés par interactions électrostatiques entre les groupes cationiques du corps polymère et les sites chargés négativement à la surface de l'argile. Dans ce cas, $\epsilon \gg 1$ kT et $p > 0{,}7$, menant à un effondrement presque complet de la chaîne polymère sur la surface. En effet, au delà d'un niveau donné d'adsorption, un renversement de charge peut se produire en le fait que le système argile-polycation se conduit effectivement comme un échangeur d'anions. Peu d'adsorption se produit avec les corps polymères chargés négativement (polyanions) à cause d'une répulsion de charge initiale entre le corps polymère et la surface argileuse. Un pH acide, une force ionique élevée et la présence de cations polyvalents dans le système accroit et promeut l'adsorption de polyanions. Des corps polymères et des polycations peuvent entrer dans l'espace interfeuillet des silicates en expansion à couches du type 2:1, mais les polyanions ne s'intercalent généralement pas.

Les interactions des argiles avec des corps biopolymères tels que des protéines, des acides nucléiques et des polysaccharides peuvent être rationalisées en des termes semblables. Lorsque l'intercalation se produit, le corps polymère interfeuillet est stabilisé d'avantage face à la dégradation microbiale (enzymatique), menant à des applications pratiques de complexes argile-polymère en tant que flocculants et de conditionneurs de sols. Les polyanions sont de bons flocculants à cause de leur grande "distance étreignante," tandis que les corps polymères sans charge sont de meilleurs conditionneurs de sols parcequ'ils peuvent s'étendre par dessus des particules argile/sol adjacentes comme une couche de peinture. [D.J.]

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