

2 Colloid Chemical Properties of Humic Matter

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2-1. INTRODUCTION

Since van Bemmelen (1) in 1888 first recognized soil humic matter as a colloidal substance, literature on the colloidal properties of humic matter has formed an interesting part of the history of colloid chemistry. It is impressive to learn from Odén's (2) 1919 monograph on humic acids of the great progress made by that time. In his preface Odén mentions that from the viewpoint of pure chemistry there were no criteria of purity of the substances studied and therefore the results were disputable. Odén very properly objects that, "should we wait till chemistry had supplied us with methods to get amorphous, non crystalline and difficultly soluble substances in strictly pure form, the research of natural substances could be laid aside for the coming hundred years." Nowadays it is assumed on good grounds—see, for example, Dubach and Mehta (3)—that there is no "pure" humic acid in the sense of a substance consisting of a collection of molecules of identical structure and weight, so we can continue to use the plural form. Nevertheless, we have a rather clear picture of several colloidal properties of humic matter.

More than two decades ago the ideas that the particles of a substance in colloidal solution consist of rather compact, polymolecular aggregates and

that the stability of hydrophilic colloids is caused by an electric double layer plus a mantle of hydration water were abandoned. It became generally accepted that for many organic substances the sol state represents principally an equilibrium state reached spontaneously by dissolution of the dry colloid in an appropriate solvent. The particles, which may be coiled long-chain molecules, two- or three-dimensional cross-linked macromolecules, or reversible aggregates of such molecules, may be present as more-or-less swollen, loosely built structures. An electric charge on the particles generally originates from ionization of acid or basic groups, regularly distributed throughout the particles (i.e., not present only at the surface). This ionization often causes an extra expansion of the particles as a result of mutual repulsion of equally charged groups and usually promotes the dissolution. For these colloids flocculation can often simply be explained by a repression of the ionization. To a certain extent humic matter appears to fit quite well into this picture and many of its colloidal properties can easily be understood on the basis of these concepts (4).

In this chapter the term "humic matter" is used in the sense originally proposed by Page (5), namely, the "dark-colored high-molecular colloidal organic matter" formed during the decomposition of organic residues. The part that is soluble in cold, dilute alkali and is reprecipitated by acidifying is referred to as "humic acids." The research on "fulvic acids," which do not precipitate on acidification, is not discussed here as their particle size generally is below the range of that of colloids.

Studies on the colloidal properties of humic matter have mostly been performed either on organic soils in their entirety or on humic acids extracted from peats or mineral soils. The first concerns mainly swelling and shrinking and ion-exchange behavior. Colloid-chemical investigations of humic acids have been performed mostly on sols or suspensions and comprise molecular weight determinations and fractionation by partial flocculation, chromatography, electrophoresis, and so on. Some of the literature on these aspects is also reviewed by Felbeck in Chapter 3.

2-2. PARTICLE SIZE, SHAPE, AND STRUCTURE

A. Particle Size

In sharp contrast with the field of mineral soil components, few studies have been made on the particle-size distribution of soil organic matter in its entirety. Russian investigators have performed most of the studies in this field. These, however, are often restricted to determinations of organic matter contents in fractions derived from suspensions of soil in water. Actually, we are dealing here with the organic matter distribution over the

mineral fractions. Usually it is not known how much free organic matter and how much organic matter adheres to mineral particles. Only where highly organic soils are concerned are more-or-less correct data regarding the particle-size distribution obtained.

Soil organic matter is polydisperse, and more than one method is required for particle-size analysis. For peat, Churaev (6) recommends wet sieving for particles down to 250 μ , gravimetric sedimentation analysis for the size distribution between 250 and 1 μ , and electron microscope analysis for particles smaller than 1 μ . The peat is suspended in water, no peptizing agents being added. A distribution curve obtained is reproduced in Figure 2-1. According to Churaev, these curves usually show at least two maxima, one or more (depending on botanical origin) for coarse particles, consisting of undecomposed or partly decomposed plant remains, and one for humic matter in the range 0.2–1 μ .

Although no exact data are available for mineral soils, it is almost certain that the latter maximum is not the same; interaction with mineral particles as well as a different humification process (involving microflora and microfauna) presumably exerts a profound influence. Strong indications in this direction are obtained from micromorphological studies of thin sections; for example, those performed by Jongerius and Schelling (7).

The humic matter fraction obtained by Churaev by suspending peat in water consists of microaggregates as revealed by addition of a peptizing agent such as a diluted alkali hydroxide or pyrophosphate solution. We are not aware of publications concerning a particle size distribution of that part of the humic matter that does not go into solution under these circumstances

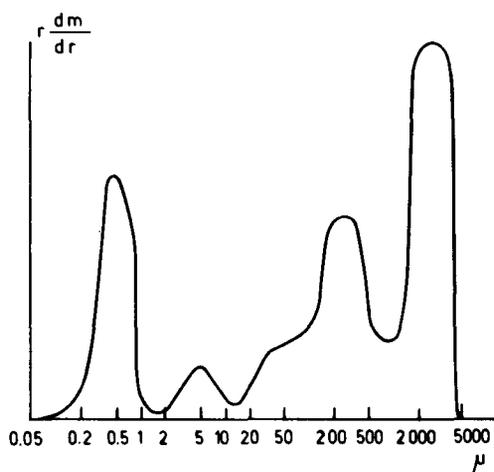


Fig. 2-1. Particle size distribution curve of a sample of *Scheuchzeria-Sphagnum* peat. After Churaev (6).

(the so-called "humins"). However, much effort has been made to determine particle sizes and molecular weights of the humic acids that go into solution upon addition of alkali or other peptizing agents.

Before 1960 there was a great discrepancy between the results of particle size measurements by electron microscopy and molecular weight determinations for humic acids. This was particularly true in the case of "number-average" molecular weights as determined by cryoscopic or osmotic methods. For example, Wiesemüller (8) found average molecular weights of about 2,000 by isothermic distillation, whereas the electron microscope revealed particles with a diameter of 100 Å, which indicated molecular weights of more than 20,000. Particle radii of 60–80 Å, derived from electron microscope studies, were reported by Flaig and Beutelspacher (9) in 1951, and these results were confirmed by others (10). From a study of the electrophoretic mobility of humic acids, Jurion (11) recently deduced diameters of about 60 Å.

This great gap between molecular weight determinations and particle diameter measurements was largely explained with the aid of fractionation studies with Sephadex (Mehta et al., Ref. 12; see also Chapter 3) and by sedimentation analyses with the ultracentrifuge. These studies showed that humic acids represent polydisperse systems with a wide range of molecular weights. According to studies with Sephadex, these weights vary from a few 1,000 to more than 100,000. Hence there arose considerable doubt about which methods give correct values. [For a criticism of the cryoscopic method, see Mehta et al. (12); for vapor pressure osmometry, see Schnitzer and Skinner (13).] Even when a method gives essentially correct values for average molecular weights, this information is of a rather restricted value. A much better characterization is obtained by determining molecular weight distributions.

By ultracentrifugating humic acids in the presence of sodium chloride, in order to eliminate retardation of the sedimentation by small "counterions" lagging behind the large organic anions, Flaig and Beutelspacher (14) recently found particle radii that were nearly equal to those they had calculated from electron microscope observations, namely, about 70 Å; particle weights were in the range 60,000–80,000. When the above-mentioned retardation effect was not eliminated, the apparent particle radii were 47–38 Å, and decreasing with increasing pH (i.e., increasing ionization), and the corresponding apparent particle weights decreased to 4,850 and 2,050, respectively. These results underline the extreme importance of allowing for electroviscous effects in precipitation or viscosity measurements with humic acids.

B. Particle Shape

An advantage of the otherwise complicated ultracentrifuge studies over that of fractionation with Sephadex is that data are also obtained with

respect to the shape of the particles. Flaig and Beutelspacher (14) concluded that humic acid particles are approximately globular, which agrees with previous electron microscope and viscosimetric measurements. These experiments were, however, made in absence of neutral salts. When performed in the presence of sodium chloride, it appeared that shapes deviate from globular. Piret et al. (15) also concluded from viscosity measurements in presence of sodium chloride that humic acids molecules are nonspherical. Assuming prolate ellipsoidal particles and a hydration of 1.0 g per gram anhydrous solute, they calculated an axial ratio of 6.8. Unfortunately, it is difficult to say whether or not their data are correct, as they performed their measurements with a rather crude sample of humic acids. It seems, however, safe to say that at least part of the humic acids molecules in solution show ellipsoidal shapes. According to Wershaw et al. (16), the particles not only vary in size but also in shape. In this connection it is also worthwhile to mention that Visser (10,17) concluded from viscosity and electron microscope measurements that molecular weights as well as the shapes of humic acid particles may undergo changes during the humification process.

A peculiar property of humic acids observed by Flaig and Beutelspacher (9) may be mentioned, namely, the formation of stringlike agglomerates of primary particles upon flocculation.

C. Particle Structure

There is contradictory chemical evidence regarding the structure of humic acids. For example, Mendez (18) and Hansen and Schnitzer (19) concluded that humic acids consist of isolated aromatic rings linked to each other by aliphatic chains or saturated cyclic or hydroaromatic units. Cheshire et al. (20), however, decided on a polycyclic aromatic "core" with aliphatic and isolated phenolic compounds attached to it. This point is also discussed by Hurst and Burges (21). It may be added that this contradiction is also reflected in results from x-ray and electron diffraction studies of humic acids. Kasatochkin et al. (22) conclude, among others, from x-ray spectra, that humic acids consist of a plane skeleton of highly condensed aromatic nuclei with side radicals, containing aliphatic groups, amide and carboxyl groups, and so on, Visser, however, concluded, as several others had before, that humic acids are entirely amorphous substances and that the apparent crystallinity shown by electron diffraction patterns is attributable to mineral "impurities" (17). Such contradictory evidence is so persistently reported that the question whether perhaps both types of structures occur is justified. The first might belong to humic acids formed at "weathering" of carbonized "organic matter" or of graphitic material. The other might belong to conversion products of lignin and to condensates of microbial metabolites. That the

latter two products have a highly conjugated polycyclic aromatic core seems rather improbable. Modern formulations of lignin, reviewed by Pearl (23), do not suggest that such an intensive condensation is likely. Freudenberg and Neish (24) are of the opinion that the main part of the structure (of lignin) should be rather resistant to degradation and would be expected to remain large in size. Further, metabolic products of lignin may, and presumably do, give rise to three-dimensionally cross-linked structures, but not to regularly formed polycyclic compounds with anthracene-like structure. This is consistent with the views of those who concluded from their electron microscope investigations that humic acids are amorphous, the particles having a more-or-less open, spongy structure. To a certain extent this concept is corroborated by the observations of van Dijk (25), namely, that in a humic acid solution all acid groupings were able to bind very large organic cations, for example, methyl quininium hydroxide, apparently without steric hindrance.

Finally, mention should be made of the interesting observation of Flaig and Beutelspacher (26) that particles of nitrogen containing humic acids, prepared from hydroquinone, were electronoptically denser (had a more cross-linked structure) than the corresponding nitrogen-free humic acids.

2-3. BEHAVIOR WITH WATER

A. Shrinkage on Drying and Reswelling in Water

A subject often disregarded in discussions of the colloidal properties of humic matter is its behavior toward water. In this section only sorption of water vapor and swelling and shrinking are discussed.

It is well known that drying of fresh peat is attended by considerable shrinkage and that neither the original water content (see Fig. 2-2) nor the original volume of the peat sod is regained when the dry peat is brought into contact with water. Thus to a certain extent the shrinkage is irreversible. For example, van Dijk and Boekel (27) found that the total shrinkage on drying may amount to 80 vol. %, whereas the reswelling of a strongly decomposed peat may be limited to 10% of the original volume. From the fact that shrinkage is generally greater the more the peat is decomposed it follows that this property is particularly one of humified matter. However, even the most decomposed peats and, as will be discussed, humic acids show limited reswelling. Apparently this property of peat cannot be ascribed solely to the presence of nonhumic matter. Swelling of humic matter is another indication that it does not, or at least not completely, consist of globular particles nor of particles with a regular three-dimensional structure. However, perhaps the possibility of stringlike aggregates (9) behaving like giant linear macromolecules in showing some swelling, should not be ruled out completely.

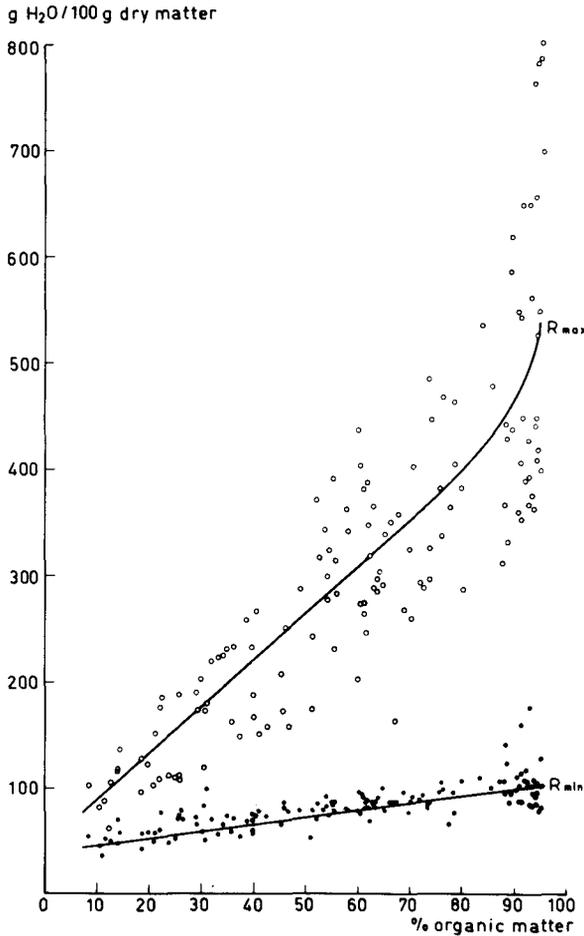


Fig. 2-2. "Centrifuge moisture equivalents" (remaining water content after centrifugation at $1000 \times g$) of fresh peat (R_{max}) and of peat which has been dried, ground, and resaturated with water (R_{min}), as a function of organic matter content. After Hooghoudt et al. (35).

The fact that shrinkage of humic matter is to a large extent not completely reversible, that is, reswelling on contact with water is limited, deserves discussion. In the older literature, poor wettability of dry organic matter was often considered the primary cause of this irreversibility (see, for example, Brüne, Ref. 28). This poor wettability is generally ascribed to the presence of adsorbed air on the dry solid (29-32), films of iron humate (33), and also to the presence of fats, resins, or waxes (e.g., Ref. 34). Hooghoudt et al. (35), however, believe that the poor wettability is an attendant effect of drying of

peat but not the reason that reswelling is limited. Rather, they assume the phenomenon to be primarily the result of the formation of secondary bonds, particularly hydrogen bridges, acting as cross-links in the contracted gel network. Such bonds are not easily disrupted by the dissolving action of water. If hydrogen ions or di- and polyvalent cations are "replaced" by alkali or ammonium ions, reswelling of dry humic matter is strongly enhanced and may even lead to partial dissolution. In the literature this phenomenon is sometimes described as "osmotic swelling."

Important differences in water retention capacity at pF 3 (see below) when the peat, before being dried, was partly saturated with different di- or trivalent cations were not found although, according to Stadnikoff (36), these ions strongly affect the coagulation velocity.

It may also be mentioned that the poor wettability of dry humic matter is an unfavorable property of organic soils but, according to Monnier (37), in clay soils it has a beneficial effect since the slower wetting of the soil results in increased structural stability.

Several schemes have been proposed for the classification of water in peat, as reviewed by Dalton (38). All these schemes are based on the manner in which water is assumed to be bound. Terms such as "capillary" or "free" water, "colloidally," "osmotically," and "chemically" bound water are used. However, there is no sharp transition between the ways in which water can be held, and these terms partially overlap. van Dijk and Boekel (27) are therefore in favor of a scheme used for mineral soils based on the free energy of the water. This is conventionally expressed in pF units where pF is the logarithm of the specific free energy when the latter is expressed in centimeters of water. In this way they obtained pF curves for peat as shown in Fig. 2-3.

A phenomenon not uncommon for organic colloids is also shown in Fig. 2-3, namely, the effect of freezing on the water retention of strongly decomposed peat (i.e., a peat for the main part consisting of humic matter). A plausible explanation is the following. A gradual growth of ice crystals in the water-saturated gel causes an expansion of volume and disruption of part of the "meshes of the gel network." This increases the average pore diameter and correspondingly decreases the free energy of water after thawing as compared with the situation before freezing. Drying of this peat, which was frozen when fresh, results in considerably less shrinkage. The contractive force exerted on the peat has become smaller. Besides, freezing may have resulted in a greater rigidity of the remaining network. The sorption of water and the reswelling of the peat is considerably greater. Thus freezing partially nullifies irreversible shrinkage.

The same kind of phenomenon can be observed with humic acids. When the "gel," obtained from centrifugation of a suspension of flocculated humic

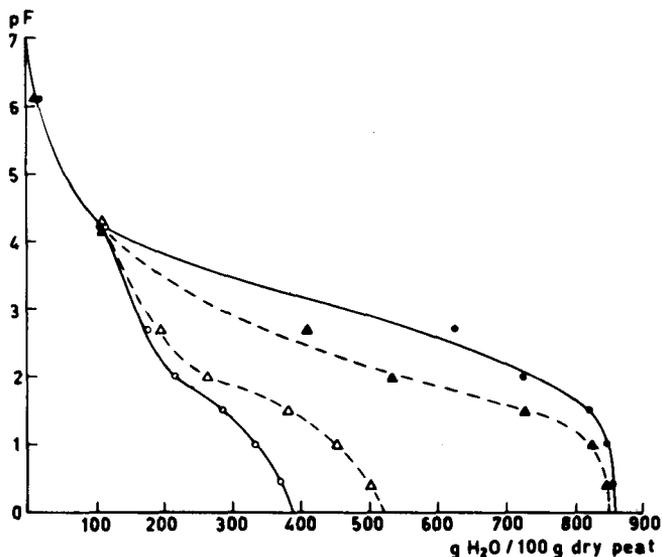


Fig. 2-3. Average pF curves of "black peat" in different conditions. ● Fresh; ▲ after freezing; ○ after drying and resaturation with water; △ after freezing, drying, and resaturation. After van Dijk and Boekel (27).

acids, is frozen and left to thaw on a Büchner funnel, the main part of the water flows off easily, leaving behind a black granular product. After drying, brittle, porous granules are obtained instead of the hard compact lumps obtained when the gel is dried without previous freezing.

It can also be observed from Fig. 2-3 that at pF 4.2 (the "wilting point") about 100 g of water per 100 g of dry peat is retained, no matter how the peat has been treated. Starting with dry peat, Hooghoudt et al. (35) obtained a similar difference between the volume of carbon tetrachloride (a nonpolar and nonswelling liquid for humic matter) and that of water retained at pF ca. 3. Thus at pF 4.2 it might be said that the remaining water is "colloidally bound" or bound by polar groups of the humic matter.

B. Sorption of Water Vapor

In the foregoing section, following the line of thought of Hermans (39) and others (40), swelling of humic matter considered adsorption (exothermic) following by dissolution (entropy gain) a process stopped only by the coherence of the solute. Chapek and Zhuravel (41), as far back as 1939, found at the saturation vapor pressure of water ($p/p_0 = 1$) a linear expansion of 9.4% for dry peat, 14.6% for calcium humate, and 30% for sodium humate. This expansion (swelling) was insignificant below a relative vapor

pressure (p/p_0) of 0.5, but increased rapidly at higher vapor pressure. Swelling was interpreted as the growing of a water mantle surrounding the solid particles as suggested for humic acids from brown coal (42). However, since the calcium ion is more susceptible to hydration than the sodium ion, the water mantle of sodium humate should be less thick than that of calcium humate. To explain this anomaly, Chapek and Zhuravel advanced the hypothesis that the swelling of hydrophilic colloids is caused by "osmotic swelling of micelles": "At $p/p_0 = 0.5$ capillary condensation sets in within the capillaries and at the spots where they touch. The water formed by condensation penetrates into the micelle owing to the difference usually existing between the osmotic pressures within and outside a micelle . . . This process continues until the elastic forces of the walls of the micelle counterbalance the osmotic swelling and until the capillaries are filled with water." This description of the swelling process has since been proved essentially valid in many cases. "In the typical macromolecular gels sorption should be regarded as a homogeneous dissolution of the sorbate in the sorbent . . ." (Hermans, Ref. 39). Just as in other dissolution processes, the sorption is governed by the enthalpy factor resulting from intermolecular forces and the entropy factor connected with molecular motion (40).

In recent years the sorption of water vapor by humic matter has not been actively investigated, although there remain some questions that deserve a closer investigation. These include effects of different base saturation and whether there are important differences between humic matter of different soils. Some recent data have been published by Beutelspacher and Nigro (43) and gathered by van Dijk (44).

Some sorption and desorption isotherms are given in Fig. 2-4. The curves with hysteresis are typical for amorphous substances showing limited swelling upon sorption of water vapor, in agreement with the observations of Chapek and Zhuravel (41). There is an effect of cation saturation in the order of $\text{Na} \approx \text{K} > \text{Ca} > \text{Ba} \approx \text{H}$. This is the same order as that found for the strength of cation binding (see Section 2-4-B). Although this should be checked for more metal ions, it is in line with the supposition that the sorption of water vapor is related to the bond strength for cations in the same way that the latter determine the solubility (and ionization) of humates in water (see below).

Mutual differences in water vapor sorption by natural humic acids of different soil types were found not to be related to nitrogen content or exchange capacity. In contrast, measurements with synthetic humic acids prepared from di- and trihydroxybenzenes gave an indication that less water is absorbed, particularly at higher vapor pressures where swelling occurs, the higher the nitrogen content of these humic acids. [An explanation might be based on the observation of Flaig and Beutelspacher (26) that the binding of

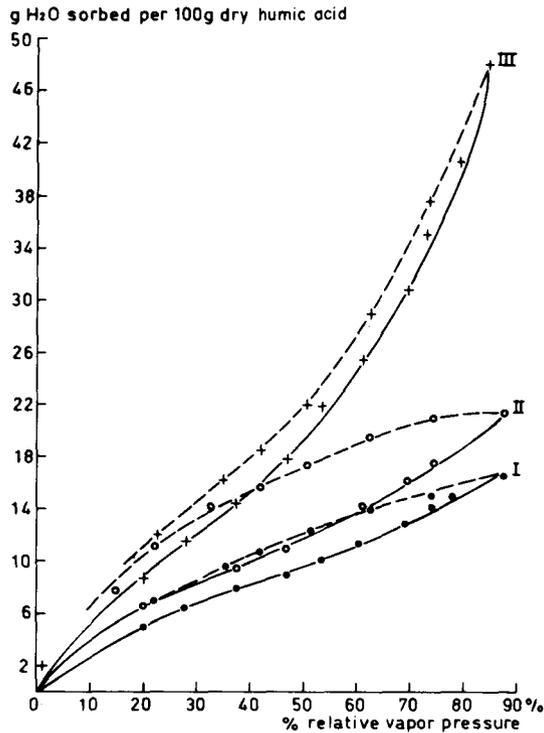


Fig. 2-4. Sorption and desorption isotherms of humic acids (I), calcium humates (II) and sodium humates (III). After van Dijk (44).

nitrogen (from ammonia) results in more cross-linked structures. In that case a higher resistance to swelling seems obvious.]

2-4. ION-EXCHANGE BEHAVIOR

In recent years much attention has been given to binding and exchange of ions by humic matter, particularly "micronutrients," ions of elements of the transition series. Plant nutrition depends on the supply of "microelements" and is therefore strongly dependent on the ion-exchange behavior of organic matter.

Most research has been focused on humic (and fulvic) acids, owing to the fact that of the total exchange capacity of the top layer of mineral soils 25–90% is a result of the presence of organic matter and especially due to its humic acid content. Mortensen has reviewed the literature up to 1962 (45), hence only the more recent literature is surveyed here, with the exception that in order to trace the development of the theoretical approach earlier papers

are occasionally cited. The literature is grouped according to the methods applied.

In many publications the terms "complex" or "chelate" are used for salts of humic acids and di- or polyvalent metal ions. It appears, however, that these terms are often confused in meaning, hence only the nomenclature of the International Union of Pure and Applied Chemistry (IUPAC) is followed. Slightly dissociated salts of humic acids and polyvalent bases are denoted as polynuclear complexes. This, however, does not stipulate the nature of the bond but only that a number of metal ions is attached to an equal number of bi- or poly-dentate ligands of one humic acid molecule. The binding of cations to negatively charged groups of an ion exchanger always involves electrostatic forces (Coulomb forces) to some extent. Such bonds may also have a more-or-less strongly covalent character. The bond between metal ions of the first transition series and chelate ligands of the humic acids is undoubtedly partly covalent.

A. Potentiometric Investigations

Upon addition of a metal salt of a strong acid to an aqueous solution of polybasic humic acids, the pH generally decreases. The magnitude of this decrease depends on the ratio of the affinities of the metal and the hydrogen ion for the humic acid polyanion and on special entropy considerations for polyanions (46).

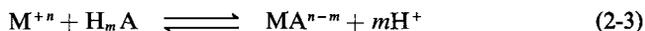
The reaction between the (hydrated) metal ion and the fully dissociated form of a polyacid can be written as



and the formation constant of this metal complex can be written as

$$K_{MA} = \frac{[MA^{n-m}]}{[M^{+n}][A^{-m}]} \quad (2-2)$$

The decrease in pH is caused by the reaction



for which the equilibrium constant is

$$K' = \frac{[MA^{n-m}][H^+]^m}{[M^{+n}][H_m A]} \quad (2-4)$$

Multiplying K' by $[A^{-m}]/[A^{-m}]$, we see that $K' = K_{MA} K_A$, in which K_A is the dissociation constant of the acid. Thus to calculate the formation constant K_{MA} of a metal humate, the dissociation constant of the humic acid must be known.

The titration curve of a polymeric organic acid was described by Katchalsky and Spitnik (46) as a generalized Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_i + n \log \frac{S}{1 - S} \quad (2-5)$$

where K_i = the "intrinsic" dissociation constant of the polymer acid (depending on the ionic strength of the solution), n = approximately a constant, and S = degree of neutralization or dissociation. Dawson et al. (47) tested this equation (to which they added a term for the ionic strength) in an investigation of the exchange of calcium for hydrogen ions in a suspension of wood peat in water and concluded that the behavior of this peat suspension deviates from that of an "ideal" polybasic acid. Good agreement would indeed have been very remarkable for such an ill-defined mixture of different organic (and other?) materials in a rather concentrated suspension titrated with calcium hydroxide. van Dijk (48) tested the applicability of this equation to humic acids titrated with sodium hydroxide, and Martin and Reeve (49) did the same for organic material extracted from soil with an aqueous solution of acetylacetone. By plotting the pH against $\log S/(1 - S)$, no linear curves were obtained, indicating that the behavior of these organic substances differs from that of linear polymers such as polyacrylic acid, for which Eq. (2-5) was derived (46).

Possible causes for this deviation are: (1) Humic acids have at least two kinds of acid groups, namely, carboxyl and phenolic hydroxyl groups; (2) it is improbable that these acid groups are as evenly distributed over humic acid molecules as is the case with polyacrylic acid (the former presumably are nonlinear heteropolycondensates), and (3) Eq. (2-5) is also invalid when there is interaction of neighboring acid groups, for example, of carboxyl and phenolic hydroxyl groups in *ortho* positions on a benzene ring (and this has not been ruled out). Posner (50) points out that in the acid region (up to pH 6.0) the titration results are fitted reasonably well the Henderson-Hasselbalch equation. However, very weak acid groups that are only titrated at a high pH have been shown to play a role in binding polyvalent cations. Consequently, using only the low " $\text{p}K_i$ " found by extrapolating the first linear part of the curve for the calculation of formation constants of metal humates gives incorrect values.

In the last decade much qualitative insight has been gained into the nature and strengths of the bonds between metal ions and humic acids by potentiometric studies. Beckwith (51,52) found that the order of decrease of pH upon addition of manganese, cobalt, and nickel salts to a humic matter suspension is the same as in the well-known series of Irving and Williams (53). He concluded that metal chelates are formed as coordination compounds with partly covalent bond character. Martin and Reeve (49) have suggested

the possibility that protons, titratable in presence of metal salts, may also originate from the hydrated metal ions and not only from the organic substances. They did not find the above-mentioned order of drop in pH. Further, they found a horizontal displacement of the titration curve in the presence of a copper salt, which could be explained simply as the formation of a "basic" copper salt. These authors are of the opinion that possibly an electrostatic interaction exists between the metal ions and the "humus polyanion" as a whole; this stabilizes the normal ion-ion binding without further specific effects in this interaction.

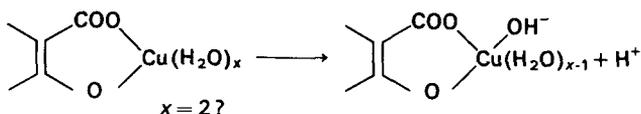
Kawaguchi and Kyuma (54) in a study confined to the binding of Ca, Al, and Fe(III) ions, found that in 0.1 *N* KCl solutions titration curves of humic acids are not influenced by the presence of Ca ions. They ascribed the effect of the addition of $\text{KAl}(\text{SO}_4)_2$ or of $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ to the Al and Fe(III) ions, however, without knowing whether these ions are indeed present as free (hydrated) ions and not in a complex form.

Khanna and Stevenson (55) found the following order of pH drop for humic acids: $\text{Mn} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$, which agrees with the Irving-Williams series. Inflection points corresponding to the formation of MOH^+ did not occur, and it was therefore assumed that these metal ions are bound in coordination compounds. From the fact that the pH drop is only small and only protons seem to be "displaced" from groups that are also titratable in the absence of these salts, they conclude that the bonds are mainly electrostatic.

Wright and Schnitzer (56) and Schnitzer and Skinner (57) found that calcium and magnesium salts did not influence the titration curves of humic and fulvic acids and nickel and copper salts did so only to a small extent. Ferric and aluminum salts had a strong effect in the sense that they caused a significant decrease of pH at the start and induced a more gradual slope of the titration curve. The curves showed no inflection points, typical of the formation of ferric and aluminum hydroxide.

Potentiometric titrations of a large number of humic acids in the presence of various metal ions have led to several conclusions (van Dijk, Ref. 58): First, metal ions are bound only to negatively charged ligands of the humic acids, in this case to ligands bearing protons titratable up to pH 11. Second, stability of the metal humates is strongly dependent on pH. Judging from the magnitude of the pH drop upon the addition of inorganic salts, at pH 5 there is not much difference in affinity for humic acids among the divalent ions Ba, Ca, Mg, Mn, Co, Ni, Fe, and Zn (in this order only slightly increasing). Pb(II), Cu(II), and Fe(III) ions, however, seem to be bound with a greater strength, increasing in this order. Aluminum ions at pH 5 seem to be subject to hydroxide formation, in contradiction with the opinion of Schnitzer and Skinner (57). Third, at a higher pH humates of metals of the first transition series are

apparently converted into hydroxy complexes with protons dissociating from water molecules covalently bound to these metal ions as exemplified by the reaction:



Hydroxy complexes with Fe(III) and Al may be formed even at a low pH.

In the order Mn, Co, Ni, Cu it is increasingly difficult to exchange these metal ions for those of the alkali or alkaline earth metals. Part of the metal ions may even be inexchangeable in this way, as for example is the case with Cu(II) ions. Fourth, the order of magnitude of the pH drop corresponds neither with that of the Irving-Williams series nor with the order of pH at which oxide hydrate formation occurs in solutions of inorganic metal salts. Schnitzer and Skinner (59) also arrived at the former conclusion when investigating fulvic acids. In the reaction involving copper given as an example above, it is assumed that the two ligands acting together in binding metal ions may be neighboring carboxyl and phenolic hydroxyl groups. That this situation occurs although presumably not exclusively, is confirmed by investigations of Himes and Barber (60), Schnitzer and Skinner (61), and Davies et al. (62).

An exchange of OH^- in the hydroxy complexes with other anions (as, for example, phosphate) does not seem improbable. By this reaction, the low and medium fulvic acid-metal phosphate complexes studied by Levesque and Schnitzer (63) might be formed.

B. Ion-Exchange Methods

1. Alkali and Alkaline Earth Ions

Scheffer and Ulrich (64) give some ion-distribution curves for alkali and alkaline earth ions calculated from the experimental data of Zadmard (65), which were obtained from a suspension of strongly decomposed peat in water. These curves show that the affinity for these cations usually increases slightly with decreasing radius of the hydrated ion and very strongly with the valency of the cations. Certain anomalies may be explained in terms of the presence of different kinds of acid groups or of different kinds of ionic bonds, and also of some experimental difficulties. Jungk (66) studied the exchange of hydrogen ions of peat moss, not to be identified with humic matter, against a number of mono- and divalent cations. In general, the results of Zadmard were confirmed. However, at lower saturation K and NH_4 and at higher saturation Ca and Ba changed position in the sequence of selectivity: $\text{Na} < \text{K} < \text{NH}_4 \ll \text{Mg} < \text{Ca} < \text{Ba}$.

Jungk tested the exchange equation of Gapon (67). It appeared, however, that the Gapon exchange "constant" was far from constant and strongly depended on the relative saturation with the "inchanging" cation. This might be explained as an indication that more than one anionic group is involved in the exchange reaction or that there is a specific (nonelectrostatic) interaction with one of the cations. In the Gapon equation, however, it is also assumed that the total number of exchange sites participating in the exchange equilibrium is constant. As Jungk rightly observes, this is not the case, since with increasing exchange of H^+ ions, that is, with increasing pH, the number of exchange sites also increases. Thus to be able to conclude whether or not there is a specific interaction with a certain cation, the dissociation constants of the acid groups involved in the exchange process have to be known.

Recently, Ong and Bisque (68) found a sequence for mono- and divalent ions, Li, Na, K, Mg, and Ca, with respect to their coagulating effect on humic acids, which is the same as the above-mentioned order of affinity. They observed that coagulation is attributable to the combining of cations and anionic groups of the humic acids with a reduction in the number of mutually repulsing anionic groups in the humic acid molecule; this decreases solubility of the polyacids.

2. Heavy Metal Ions

Himes and Barber (60) obtained an estimate of the stability of the zinc-organic matter complex by adding radioactive zinc ions to a soil suspension together with known chelation compounds. They then measured the amount of zinc not adsorbed by the soil. A drawback of this method is that the possibility of the formation of mixed complexes may confuse the issue. An interesting observation of these authors is the slowness of the exchange of adsorbed Ag^+ ions, indicating a role, at least partly, of a covalent bond in binding. A further indication of mixed-bond types in interactions between "trace element" cations and humic acids is also the observation of Basu et al. (69) that "adsorption isotherms" of humic acids against Cu^{2+} , Zn^{2+} , Ni^{2+} , and Mn^{2+} are generally somewhat higher than the corresponding "release isotherms."

Broadbent et al. (70-74), in a series of publications, call attention to the fact that not all ions of a certain metal adsorbed by soil organic matter or by humic acids are bound with equal strength. They removed successive fractions of metal ions by washing with solutions of different acids and acid concentrations. Different bond strengths are assumed to be connected with the occurrence of different (three or more) ligands. To obtain more information about the identity of these ligands, a comparative study was made with several simple organic acids (often monobasic acids) or buffer solutions. Their conclusions

are open to controversy because they did not take into account the fact that polybasic acids even with only one kind of acid group show a range of dissociation constants, did not consider an electrostatic field effect of the polyanion as a whole, and did not allow sufficiently for the possibility that neighboring carboxyl and hydroxyl groups act as bidentate ligands. Nevertheless, these investigations show clearly that part of the micronutrients may be very strongly fixed to humic matter and more information is given than when only average "retention factors" for micronutrients are determined (see, for example, Szalag and Szilágyi, Ref. 75). This became evident from investigations of Ennis and Brogan (76), which showed that only the most strongly bound copper (not removed by washing with 1.0 *N* HCl) was virtually unavailable to oat plants.

It may be mentioned that there are other factors that may affect the exchangeability of cations. For example, after drying a copper-peat complex and resuspending it in water, part of the Cu ions appeared to exchange with greater difficulty (van Dijk, Ref. 77).

In recent years a number of investigators (59,78,79) have used the ion-exchange technique developed by Schubert (80) to determine stability and formation constants of the complexes between metal ions and soil organic components. In this way Randhawa and Broadbent (78) calculated the log stability constant for a zinc-humic acid complex to be 4.42 at pH 3.6, 6.18 at pH 5.6, and 6.80 at pH 7.0. Courpron (79), however, using the same method, found a considerably lower log stability constant for zinc humate at pH 5.0, namely, 2.87, whereas at this pH a value of 7.00 was calculated for the Cu(II) complex. For the corresponding zinc- and copper-fulvic acid complexes at pH 3.5 values of 2.83 and 3.23, respectively, were calculated. Schnitzer and Skinner (59), however, obtained values of 1.73 and 5.78 for these complexes at pH 3.5, and 2.34 and 8.69 at pH 5.0. In all three laboratories (78,79,59), the measurements were made under comparable conditions. It may be questioned, however, whether the differences found can be fully ascribed to different origins of the humic and fulvic acids. Van Dijk (58) failed to find significant differences among humic acids of widely different soils, notwithstanding variations in nitrogen contents and ratios of stronger to weaker acid groups. Clark and Turner (81) have criticized the method of calculation of stability constants from the data derived from the ion-exchange method of Schubert. They emphasize that these constants cannot be calculated from a simple mononuclear equation unless the number of moles of the organic components involved in a complex is an integer. In the above-mentioned publications, however, this number varies from about 0.50 to 2.00.

Experiments of the kind carried out by Himes and Barber (60) involving humic acids and some known chelators and copper have also been performed in our laboratories (82). The data obtained suggest a log stability constant for

copper humates at pH 6 of about 7, which agrees quite well with that calculated by Coleman et al. (83) for a copper-peat complex, namely, 6.5, and with that found by Courpron (see above). The results with different amino acids (potential carriers for micronutrients from humic matter to plant roots) were not quite consistent, possibly because of the formation of mixed complexes.

In summary, at present much is known qualitatively about complexing of metals with soil humic substances, but exact and unassailable data regarding their conditional formation constants are still lacking. An intriguing question in this context is whether the metal ions present in the complexes are partly reduced to a lower valency as suggested by Kleist (84) and by Randhawa and Broadbent (78). The extent to which the presence of stable free radicals in humic acids plays a role is also unknown (Kleist, Ref. 85).

2-5. CONCLUDING REMARKS

That molecular and aggregate structure, sorption and swelling, and ion-exchange behavior of humic matter are interrelated properties has been emphasized. As is well known, the exchange capacity of organic soils is dependent on the degree of swelling. Less well recognized, however, is the fact that selectivity of cation binding generally is influenced both by the degree of swelling and by the degree of cross-linking of the molecules, and vice versa. A property not discussed here is the interaction between organic and mineral soil components, which undoubtedly also influences the properties mentioned.

For a better prediction of ionic equilibria in the soil, as well as for a better understanding of the genesis and stability of the soil structure, the study of these interrelationships still constitutes an important field for future research.

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