Precipitation of Humic Substances from Aqueous and Alkaline Solutions under the Action of Electrolytes: A Review

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Abstract—The precipitation of humic substances by electrolytes from aqueous and alkaline solutions occurs in two stages: the first is the transformation of true solutions into colloidal solutions, and the second is the decrease in the aggregative stability, the adhesion of particles, and the formation of sediment. The term *coagulation*, which is commonly accepted in colloid chemistry, is most suitable for the characterization of the above processes because the formation of the sediments of humic substances is of colloid-chemical nature. Methods for the determination of a coagulation threshold are not standardized; therefore, its values for the same materials determined by different researchers were different. The coagulation thresholds of the humic acids of solid fuels are very typical for different stages of metamorphism, and they adequately reflect the nature of fossil fuels.

PRECIPITATION OF HUMIC SUBSTANCES IN CHEMICAL-ENGINEERING AND NATURAL PROCESSES

Precipitation occurs upon the addition of electrolytes, for example, salts or acids, to the aqueous and alkaline solutions of lithium, sodium, potassium, or ammonium humates [1–3, 9, 19, 25, 63, 50, 72–75, 78, 83, 103]. The interaction of the solutions of humic substances with electrolytes is of wide occurrence in many chemical-engineering and natural processes. Thus, humic acids (HAs) are precipitated from the alkaline extracts of peat, brown coal, sapropel, soil, or other humified materials by mineral (hydrochloric, sulfuric, etc.) acids. For the isolation of fulvic acids (FAs), barium hydroxide is added to the acid filtrates after the precipitation of HAs; the resulting barium fulvates are precipitated, and this makes it possible to remove the impurities of other organic substances from the FAs.

In a technology for the production of effective water-soluble humic preparation additives to geotechnological solutions, HAs are initially precipitated from the alkaline extracts of peat by a mineral acid, and the remaining acid solution is alkalized and calcium fulvates are precipitated in an alkaline medium [6, 105]. This makes it possible to decrease many times the volumes of humic preparations transported to the sites of the underground or heap leaching of rare and scattered metals.

In a technology for the production of biologically active humic trace element fertilizers, the solutions of humic substances react with the salts of zinc, manganese, copper, and other metals with the use of processes that ensure the occurrence of trace elements in soluble forms accessible to plants [58–61].

Humic substances almost everywhere occur in natural water [127]; they are harmless to the health of human beings and animals. Moreover, the preparations of humic substances are used in medicine, balneology, and cosmetology [11, 65]. The concentrations of humic substances in river and lake waters vary from 1 to 100 mg/L depending on catchment areas; however, they most frequently contain about 10 mg/L FAs and about 3 mg/L HAs [8, 24, 124, 127]. If the dissolved humic substances are not removed from water, organic chlorine-containing compounds, for example, chloroform and dibromochloromethane, which are dangerous to human health, are formed from safe humic substances in water treatment processes for the production of drinking water, namely, upon chlorination [84]. In order to avoid the formation of harmful organic compounds, the humic substances are removed from water by coagulants before chlorination; aluminum sulfate, iron(III) chloride, and clays are the most widely used coagulants [8, 115, 116]. The capability of humic substances for the formation of precipitates with the ions of polyvalent metals and colloidal particles is used in these technologies. The principle of the method is based on the fact that the dispersed particles of humic substances in an aqueous medium have a total negative charge from −15 to −26 mV [83], and the coagulants bear a positive charge; therefore, their

interaction leads to coagulation [8, 115, 116], and humic substances are removed from water after the separation of the sediment.

The capability of humic substances for the formation of precipitates with polyvalent metals is used in water treatment technologies and for the solution of problems related to the removal of heavy metals by their precipitation upon the addition of the solutions of humic substances or alkaline peat suspensions to contaminated water [42, 43, 45, 57, 58, 62, 81]; this is especially promising for the precipitation of nonferrous metals from the liquid wastes of electrodeposition processes.

The aqueous and alkaline solutions of humic substances are used for the stabilization of drilling mud [16−18, 67, 83] and clay cake removal from boreholes [35], where they interact with salts and clay minerals. Technologies for the production of peat−alkali reagents [18], dry sapropelic powder [66], and a dry water-soluble humic preparation [105] were developed for these purposes.

The colloid-chemical processes of the interaction of humic substances with highly dispersed clay minerals and salts are of fundamental importance for the formation of the agriculturally valuable structure of soils, as evidenced by the fundamental works of Gedroits [31, 32], who was the founder of a theory of soil colloids. The formation of humic organomineral substances in soil was found experimentally; the films of these substances cover the fragments of minerals [107−109, 119, 120]. In this case, mineral particles with sizes smaller than 0.01 mm covered with organomineral films and possessing the properties of colloidal particles were referred to as primary particles [107]. The subsequent aggregation of the primary particles causes the formation of the fine structure of soils, which is favorable for agricultural plants.

It was established that the processes of soil formation, the formation of soil aggregates, the structure and other agrophysical properties of soils, their water−air conditions, and the ability of sowings to resist droughts and frost depend in many respects on the colloid-chemical processes in the soils [30, 31, 68, 104, 107−109, 119, 120]. In particular, the solutions of humic substances envelop the particles of soil minerals and form precipitates upon interaction with multivalent cations, and the resulting films of humates (primarily, of calcium humate) cement the contacting particles into larger aggregates on drying. The optimization of the colloid-chemical properties of soils is an important instrument for controlling their structure and aqueous, thermal, and other properties; in this case, the optimization of the concentration and composition of humic substances in soil plays a special role because with their deficiency the agriculturally valu-

able structure of soil is not formed even in the presence of a necessary amount of mineral colloidal particles in it. Humic fertilizers based on peat, brown coal, and sapropel are used for regulating these processes; moreover, the best results are obtained if they are preliminarily activated by converting a portion of humic substances into water-soluble forms [106, 118].

The interactions of the solutions of humic substances with electrolytes and colloidal particles are especially widespread in the water of rivers, lakes, and seas and also in soil solutions and soil water because they contain dissolved HAs, FAs, and salts. In natural water, humic substances occur in the form of salts (humates and fulvates), complex compounds with polyvalent metal ions, and associates with the colloidal particles of clay minerals, iron and aluminum hydroxides, and acids in small amounts [22, 24, 54, 55, 115]. According to Varshal et al. [22], the Earth's rivers carry 316 million tons of dissolved organic, predominantly humic, substances into seas every year; according to other published data [56], 720 million tons of dissolved organic substances and 174 million tons of mineral colloids yearly enter into the world ocean. The large-scale processes of the interaction of the solutions of humic substances with electrolytes are evident near the estuaries of large rivers, where the carried water-soluble HAs and FAs and mineral colloidal particles form organomineral sediments, predominantly with the participation of water-soluble HAs, upon mixing with salt seawater. Many metallic ore deposits were formed as a result of the deposition of the reaction products of polyvalent metals with humic substances [54, 55]. The amount of organomineral deposits at river mouths is great so that shallows are formed under their action in the estuaries and sea steps back; the new portions of formed sediments are deposited on both the shallows to increase the deposited layer and in new sea areas to gradually form the soils of river deltas. Extensive territories with the fertile soils of the Nile, Indus, Ganges, Volga, Danube, etc., River Deltas were formed in this manner [27, 56]. These processes occurred for millions of years; therefore, it is possible to say without exaggeration that the biogeochemical accumulation of organomineral compounds as a result of the precipitation of humic substances from aqueous solutions under the action of electrolytes is a general planetary phenomenon.

HUMIC SUBSTANCE PRECIPITATION PROCESSES

The ability of the aqueous and alkaline solutions of humic substances to form precipitates on interaction with electrolytes depends on concentration, pH value, the types of cations and anions that form electrolytes, the source of raw material from which the humic sub-

stances were obtained (peat, brown coal, sapropel, soil, compost, etc.), and the method and conditions of their preparation.

The classification of the solutions of humic substances with true (molecular) or colloidal solutions is a debatable problem, and three different points of view were formed by now. The essence of the earliest of them is that the solutions of humic substances, primarily, HAs, are colloidal, in which a dispersed phase consists of molecular microaggregates (micelles) with particle sizes from 10 to 2000 Å having an interface rather than of separate molecules [5, 7, 19, 25, 63, 64, 70, 86, 88]; however this point of view contradicts the results of studies that did not confirm the colloidal nature of the solutions of HAs.

According to the second point of view, the dilute alkaline solutions of HAs are true rather than colloidal because humates occur in them as separate molecules, and they do not form aggregates with an interface. Sven Oden was the first to make this conclusion [112], and this point of view currently received wide acceptance [9, 26, 39, 41, 51, 73, 75, 83, 103, 112, 121]. The dilute aqueous and alkaline solutions of the humates and fulvates of univalent cations do not give the Tyndall cone; they are characterized by a laminar (Newtonian) flow and relate to the true solutions of typical high-molecular-weight polyelectrolytes [37, 39–41, 83, 112, 121, 122]. However, at concentrations of 4–6% or higher, the aqueous alkaline solutions of humates can form colloidal systems, which opalesce and form the Tyndall cone on transillumination [75], and they possess intrinsic viscosity and can undergo thixotropic changes at concentrations of 9% or higher; this is explained by the formation of micelles from individual molecules or gels [25, 38, 41, 49, 122].

The essence of the third point of view is that HAs form hemicolloid systems in the aqueous alkaline solutions, whose properties depend on the degree of replacement of the protons of functional groups by the ions of sodium, potassium, or ammonium; therefore, HAs can form either micelles or the true solutions of high-molecular-weight compounds with medium molecular weights [1, 20, 38, 41, 83, 121, 122, 129, 130]. This point of view places strong emphasis on the degree of replacement of the hydrogen of functional groups by univalent cations and on the role of pH in the formation of true or colloidal HA solutions. The rule of the dynamic equilibrium true solution ↔ sol ↔ gel ↔ compact aggregated state (upon the removal of a double electrical layer and solvation water) is applicable to the solutions of humic substances, and this equilibrium is shifted to the right or to the left depending on the conditions in which the humic substances occur [1, 20, 41, 83, 121, 129, 130].

Acids, salts, and other compounds of univalent and polyvalent cations can be the electrolytes that cause the precipitation of humic substances from solutions at specific concentrations. According to the theory [4, 27, 100, 125], the formation of the nuclei of a new phase via the formation of supramolecular structures precedes the precipitation, and this rule is applicable to the solutions of humic substances [75, 83]. Under the action of electrolytes or with an increase in the concentration, soluble micromosaic associates with ordered and disordered sections are initially formed in the solutions of humic substances due to the connection of macromolecules by hydrogen bonds or the bridges of polyvalent cations or due to the displacement of macromolecules from the dispersion medium by salts.

According to the current concepts of colloid chemistry and the chemistry of high-molecular-weight polyelectrolytes, the capability of the macromolecules of humic substances for association is caused by their flexibility in solution, the irregular distribution of the ionogenic and nonionogenic groups of atoms and the related presence of hydrophilic and hydrophobic fragments in each molecule, and the micro-Brownian motion of the separate fragments of macromolecules; in the aggregate, this is responsible for the micromosaicity of the resulting associates with the formation of ordered sections in individual microzones [4, 20, 27, 53, 75, 89, 100, 114, 125]. The associates in solution are characterized by the inconstancy of composition in terms of the number of associated molecules; they can fully or partially decompose and appear again in another part of the solution; however, the first consideration is that associates, as the macromolecules, do not have an interface [27, 100] because of a small number of molecules in one associate. The lifetimes of the associates of low-molecular-weight substances and high-molecular-weight compounds are 10^{-10} and to 3 s, respectively. The lifetime of the associates in the solutions of humic substances remains to be measured; however, taking into account their molecular weights, it is possible to expect that it is close to the lifetime of the associates of high-molecular-weight compounds. The associates of humates with ordered microzones are considered as the nuclei of a new phase, capable of coarsening and forming microaggregates (micelles) [34, 38, 40, 78, 83, 121]. These latter differ from associates in terms of not only a great number of associated molecules but also the presence of an interface. The action of the philosophical law of an abrupt transition from quantity to quality is clearly manifested here [28]. The most important property of the microaggregates is their ability to occur in solution at sizes smaller than 10^{-4} cm even in the presence of an interface [27, 100, 125]. According to the general the-

ory of the formation of amorphous sediments [4, 27, 100], the appearance of the microaggregates of a new phase indicates a change of the true solution of HAs to the colloidal solution, and the subsequent formation of a sediment occurs from the newly formed colloidal solution.

It is possible to recognize the following three most common versions of the precipitation of humic substances by electrolytes from the aqueous and alkaline solutions: precipitation by acids, precipitation by the salts of univalent cations, and precipitation by the cations of polyvalent metals.

Precipitation by acids. It is well known that the electrolytic dissociation of carboxyl groups occurs in alkaline solutions in the presence of OH^- ions with the formation of the negatively charged carboxylate ions $-COO^-$, which repulse from each other; therefore, the macromolecules of HAs are retained in the solution. The negative charges of the carboxylate ions are neutralized upon the introduction of H^+ ions with an acid into the alkaline solution.

In the carboxyl and hydroxyl groups of HA molecules, hydrogen atoms are bound to the strongly electronegative atoms of oxygen. In these groups, hydrogen atoms are polarized as a result of the displacement of electrons to oxygen atoms, and the state and properties of the polarized hydrogen atoms approach the state and properties of the hydrogen ions H^+. Because of this, the formation of hydrogen bonds between the functional groups of different molecules or between the fragments of one molecule becomes possible. Intermolecular hydrogen bonds are formed upon the contact of molecules; as a consequence, the soluble associates and then the microaggregates of HAs are formed. The appearance of the microaggregates with an interface is indicative of a change of the true solution of HAs into a colloidal solution. Upon the further coarsening of the microaggregates, HAs are precipitated from the colloidal solution. For example, these processes are observed under natural conditions in acidic swamp water and soil water and in the production of HAs from peat, brown coal, sapropel, etc., in manufacturing practice.

The formation of molecular associates by hydrogen bonds is widespread in natural and synthetic media. For example, sulfuric acid is nonvolatile because of the presence of strong hydrogen bonds, and formic acid occurs in the form of molecular associates even in vapor because the energy of a hydrogen bond between formic acid molecules is 66.9 kJ/mol [27, 54, 117].

The energy of hydrogen bonds in HAs remains to be evaluated, but it is obvious that it is sufficient for the strong retention of the molecules in associates and aggregates without dissolution in an aqueous acidic medium. In order to dissolve the molecules of HAs, it is necessary to destroy hydrogen bonds between them; this is achieved by the creation of a neutral or alkaline medium with the replacement of the hydrogen of carboxyl groups by the univalent cations of sodium, potassium, ammonium, etc.

However, the formation of hydrogen bonds is not the sole reason for the precipitation of HAs in an acidic medium. Other reasons that facilitate their precipitation are a high molecular weight and the presence of hydrophobic fragments in the molecules of HAs. It was experimentally found that the humic substances of peat have molecules with the predominance of both hydrophilic and hydrophobic fragments [38, 63, 85, 87]; the capability for dissolution and precipitation depends on a ratio between them. The hydrophobic fractions of the HAs of peat and the FAs are about 50–60 and no higher than 5%, respectively. In connection with this, only HAs are precipitated in an acidic medium, whereas FAs remain in solution because the most hydrophilic fractions account for 95–96% of their weight and a great number of functional groups ensures the mutual repulsion of FA molecules in the acidic medium to prevent the formation of insoluble aggregates [39, 64, 75, 83, 93].

Precipitation by the salts of univalent cations. The mechanism of HA precipitation from neutral or alkaline solutions by the salts of univalent cations is completely different. In this case, the role of hydrogen bonds between the macromolecules of HAs is secondary, and precipitation occurs by a salting-out mechanism.

The salting out of high-molecular-weight polyelectrolytes, which include humic substances, occurs upon the introduction of salts, whose solubility is much higher than that of a polyelectrolyte, into their solutions. The neutral salt introduced into solution actively interacts with the solvent to weaken the interaction of the solvent with the polyelectrolyte, which is displaced from the solution and precipitated [27, 29, 100, 125]. The salting out of proteins from solutions can serve as a typical example [53].

Upon the introduction of the salts of univalent cations, for example, NaCl, into an alkaline solution of humates, a substantial portion of water is bound by salt ions because the hydration number of NaCl measured by different methods varies from 3.5 to 7.9 [33]. The incorporation of water molecules into the hydration shells of salt ions decreases the possibility of the occurrence of humates in a dissolved state because the amount of free water in the solution decreases, but the amount of humates does not change. Therefore, their concentration in the volume of free water increases to create favorable conditions for the precipitation of the macromolecules of humates from the solution by

forming initially soluble associates and then microaggregates, which have phase boundaries. It was established that, with an increase in the concentration of humates to >4%, the true solution changes to a colloidal solution [41], and favorable conditions for this process are created upon the introduction of NaCl into the solution of humates, whereas the microaggregates of humates adhere to form sediments upon the introduction of new salt portions into the solution. The salting-out efficiency of humic substances depends on the degree of solvent replacement by the salt. The value of pH, the temperature of solution, the concentration and composition of salts introduced into the solution, the molecular weight, and the structure peculiarities of the macromolecules of the salted-out substances exert a considerable effect on the process of salting out.

A ratio between hydrophilic and hydrophobic fragments is of crucial importance for the salting out of humates from solutions. Salting out is most typical of HAs, in the macromolecules of which hydrophobic fragments are clearly pronounced, in particular, of the HAs of soils, brown coal, and black coal and synthetic HAs obtained by the dehydration of carbohydrates with sulfuric acid. The greater the amount of hydrophobic fragments in the macromolecules of HAs, the more easily they are salted out, but humic substances with pronounced hydrophilic properties are not salted out in the presence of univalent cations. This is explained by the fact that the polar groups of humic substances are solvated in aqueous solutions and the solvation sheaths prevent the contacts of macromolecules; therefore, intermolecular interaction occurs at hydrophobic hydrocarbon fragments [27, 28]. The possibility of the association and aggregation of humic substances increases with the fraction of hydrophobic fragments in the macromolecules and vice versa, the predominance of hydrophilic components in the molecular structure prevents these processes. In connection with this, HAs of different genesis are essentially different in terms of the capability for salting out: the HAs of fossil coals are most easily salted out because their molecules are most hydrophobic; the HAs of soils are also capable of salting out, although they are less hydrophobic in comparison with the HAs of coals, whereas the most hydrophilic HAs of peat, sapropel, and composts and FAs are not salted out [15, 47, 48, 71, 73, 93, 96, 97, 101, 102, 132].

It is believed that the salts of polyvalent cations possess stronger salting out capacity than that of univalent cations because of differences in the ionic strength of their solutions [27, 53, 100]. For the solutions of high-molecular-weight compounds, the following lyotropic series of cations and anions were arranged based on their salting out action: $Li^+ > Na^+ >$ $K^+ > Rb^+ > Cs^+$ and $SO_4^{2-} > Cl^- > NO_3^- > Br^- > J^-$ [27, 28, 100].

The salting out of polyelectrolytes occurs most easily at a value of pH close to the isoelectric point because they have the lowest solubility at this point. Humic substances are most frequently salted out at pH 7, which is close to the isoelectric points of a large portion of their macromolecules, but the examples of the salting out of HAs from alkaline solutions are also available [15, 37, 47, 48, 93, 96, 97, 132]. An increase in the temperature of solution from 18–22°C by tens of centigrade degrees leads to an increase in the solubility of HAs and counteracts salting out, and an increase in the concentration of the salt introduced into the solution, on the contrary, facilitates salting out.

The capability of HAs for salting out is used for their separation into a salted-out gray (black) fraction and a non-salted-out brown fraction [27, 37, 47, 48, 93, 96, 97, 132].

An attempt to separate the HAs of peat into these fractions was unsuccessful, although the experiments were repeated many times [15]. However, after the hydrolysis of HAs with 2% HCl, they were separated into the brown and gray fractions; this fact is indicative of radical changes in the molecular structure of the HAs of peat under the action of acid hydrolysis. Special studies showed that, in the process of acid hydrolysis, the molecular structure of HAs is rearranged in two directions: first, a portion of peripheral chains is eliminated; second, the molecular weight increases due to the occurrence of condensation processes. As a result these and, possibly, other processes, the salted out fraction is artificially synthesized in the composition of peat HAs regardless of when acid hydrolysis was performed: before or after the isolation of HAs from the raw material. If HAs obtained after the acid hydrolysis of peat are fractionated in accordance with a published procedure [82]; it is possible to arrive at an erroneous conclusion on the presence of a salted out fraction (gray HAs) in their composition. The concentrations of hydrolyzable substances in the HAs of valley peat, high-moor peat, and sapropel are about 25–40%, to 17–23% [9, 15], and 54–76% [13], respectively, which are much higher than those in the HAs of soils and brown coals [93, 66, 71–75]. A large quantity of the hydrophilic fragments of HAs is concentrated in the composition of the hydrolyzable substances, and the residue after hydrolysis is relatively enriched in the hydrophobic fragments (aromatic nuclei and hydrocarbon chains), as confirmed by IR-spectroscopic data. Thus, because of acid hydrolysis, the macromolecules of peat HAs become more hydrophobic, in comparison with the initial HAs; therefore, they are

easily salted out. The absence of the salted out fraction of gray HAs from peat is principally important both for the knowledge of the genesis of peat, brown coal, and black coal and for practical applications in the production of growth stimulators, dyes, complex-forming additives, etc.

FAs are not salted out because they are very hydrophilic due to the presence of a large quantity of polar functional groups and weakly manifested aromatic moieties of the molecules [93], and also the capability of associates for recharging by absorbed cations [83, 30].

However, in general, the salting out the HAs of soils and fossil coals can be considered an effective method for their fractionation, and corresponding methods for the separation of such HAs into fractions were published in [37, 47, 48, 93, 96, 97, 132].

Precipitation by polyvalent cations. The following terms, which characterize the precipitation processes of humic substances from aqueous alkaline solutions under the action of polyvalent cations: coagulation [5, 7, 88, 103, 133], precipitation [50, 79], aggregation [75], and structurization [83]. Using one or another term, specialists attempted to describe the essence of the processes that lead to the formation of precipitates. For the onset of precipitation, the concentration of an electrolyte introduced into a solution of humates should be higher than a certain value, which is referred to as a coagulation [7, 133], precipitation [50, 79], aggregation [75], or structurization threshold [83].

The variety of terms testifies about the ambiguity of the views of researchers on the mechanisms of precipitation. For understanding the processes of precipitation in the solutions of humates, it is necessary to consider the essence and special features of each of the terms named above.

Coagulation is the term used for the designation of precipitation in colloidal solutions. Coagulation is the process of the adhesion of small particles into larger structural formations under the action of intermolecular (not chemical) forces [27, 100, 125]. Coagulation can occur as a result of the aging of colloidal solutions and changes in the dispersed phase concentration and temperature under the action of light, electrolytes, etc.
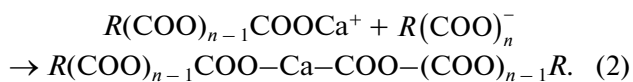
It is well known that colloidal particles are retained in solutions because of the presence of a double electrical layer and the regions of solvation. According to the Derjaguin theory, solvate layers prevent the adhesion of colloidal particles due to the appearance of disjoining pressure [27, 100, 125]. In this case, it is not necessary for the solvate layers to completely cover colloidal particles; frequently, solvation monolayers that occupy 40−60% of the surface of colloidal particles are sufficient for stabilization [100]. Because of the anisodiametricity of HA particles and the uneven

arrangement of polar groups, around which solvation monolayers are formed as a result of dipole interaction, it is likely that the solvate layers of HAs are interrupted. This is confirmed by the alternation of hydrophobic and hydrophilic fragments in the molecules; moreover, the ratios between them are different in HAs of different origin; therefore, the solvation values are different: from 3−5 to 12−14 g of dispersion medium per gram of HA in peat [9, 10, 25, 38, 40], from 1.2−2.5 to 3.0−6.8 in sod-podzol and chernozem soils [25, 93, 95], and from 4.9 to 17.4 in sapropel [101]. The process of the adhesion of particles begins because of a change in a balance between the energies of their attraction and repulsion as a result of a change in the charge of a double electrical layer upon the introduction of an electrolyte into the colloidal solution. According to the Schulze-Hardy rule, the coagulating power of ions charged oppositely to the surface of colloidal particles increases with the valence of ions, and ions are arranged in the following order with respect to this property: univalent < bivalent < trivalent < tetravalent. However, there is no linear dependence because a number of conditions affects the coagulation of colloidal solutions by electrolytes: concentration, temperature, mechanical actions, etc. [27, 100, 125]. According to the Derjaguin−Landau−Verwey−Overbeek (DLVO) theory, the electrolytic coagulation threshold depends on the sixth degree of the valence of a cation [27, 100, 125]. An increase in the precipitating action of cations with the valence of metals in the salts used for the precipitation of humic substances from 0.02% solutions was experimentally found in the alkaline solutions of the sodium humates of soils [2, 66] and peat [128]. At the same time, with the same valence, the Mg^{2+} ions more weakly precipitate humates than the Mg^{2+} ions and even more weakly than the Ba^{2+} ions [2, 14, 70−76, 103].

In a number of publications, the terms *coagulation* and the *coagulation threshold* of HAs were considered critically, and other terms were proposed for describing the essence of this phenomenon [50, 75, 79, 83].

The term *HA precipitation* is much wider in its content than the term *coagulation* because it is applicable to not only colloidal but also true molecular dispersion solutions. According [50, 51, 79], the precipitation of humic substances from solutions occurs not only due to the action of intermolecular forces but also due to the forces of chemical interactions between humates and polyvalent cations, in particular, as a result the occurrence of an ion exchange reaction. The interaction of the alkaline solutions of HAs with the salts of barium, calcium, and other metals can be represented as an exchange reaction with the formation of complexes of two or more HA molecules bound through a

bivalent cation. Larina and Kasatochkin [79] presented this reaction in the following form:

$$R(COO)_n^- + Ca^{++} \rightarrow R(COO)_{n-1}COOCa^+, \quad (1)$$

$$R(COO)_{n-1}COOCa^+ + R(COO)_n^-$$
$$\rightarrow R(COO)_{n-1}COO-Ca-COO-(COO)_{n-1}R. \quad (2)$$

According to Eq. (1), the calcium ion interacts with the carboxyl group to form a salt; in this case, one valence of the calcium atom remains free; therefore, it interacts with another molecule. Thus, a complex of two humic acid molecules bound through the cation is formed, as shown in Eq. (2). This process further continues according to the same reaction scheme with the gradual increase of the complex molecules of calcium humates. However, complete substitution for the valences of carboxyl groups and calcium ions does not always occur. As a rule, a portion of carboxyl groups is not replaced by calcium because of their spatial arrangement in the molecules of HAs, and it remains in the form of sodium humates; however, on the other hand, a portion of calcium ions remains with one free valence. The mixed humates of calcium and sodium are actually formed. In spite of this fact, as a result of agglomeration, complex molecules initially form associates and then aggregates with an interface; the stability of humates in solutions decreases to ensure the possibility of the precipitation of mixed calcium and sodium humates. These precipitates form rigid three-dimensional structures as a result of the appearance of valence bonds between calcium ions with the carboxyl groups and phenol hydroxyls of HA molecules [50, 79].

The authors of the above mechanism deny the possibility of applying the term *coagulation* because the dilute alkaline solutions of the humates of univalent cations are true rather than colloidal. Therefore, ion exchange occurs at the molecular level, and, in their opinion, the reason for the formation of precipitates is the agglomeration of the particles of a dispersed phase due to the interaction of bivalent cations with different humic acid molecules rather than the neutralization of the double electrical layer of microaggregates [50, 51, 79].

The agglomeration mechanism of the particles of a dispersed phase by means of calcium bridges was confirmed by the experimental determination of changes in particle sizes by gel filtration upon the introduction of calcium chloride into the alkaline solutions of peat humic acids [12]. In the initial solution of lithium humates from wood–cane peat, the differential molecular-weight distribution curves exhibited two maximums corresponding to 25000 and 175000 Da, whereas the maximums shifted to the high-molecular-weight region with the average molecular weights of 125000 and 250000 Da, respectively, upon the introduction of 46 mg-equiv of $CaCl_2$ per liter of humate

into the solution. Analogous results were obtained for the humates of cotton grass peat: after the introduction of 27 mg-equiv of $CaCl_2$ per liter of solution, the molecular weights increased by a factor of 3–5. In both cases, the associates of mixed calcium and lithium humates were formed and occurred in the solutions. Upon the additional introduction of calcium chloride, the associates increased to the sizes of microaggregates by the connection of humate molecules by means of calcium bridges as a result of an exchange reaction of univalent cations for bivalent, as a result of which true solution was converted into colloidal solution. By choosing concentrations, it is possible to obtain a colloidal solution of mixed humates, for example, of calcium and sodium with an interface between the microaggregates of humates and the dispersion medium (an alkali solution); upon the introduction of new electrolyte portions, the microaggregates of mixed humates agglomerated to form a sediment from the colloidal solution, as observed by Bambalov and Dite [12].

However, a number of facts contradict these concepts [50, 79]. One of them is the appearance of a sol long before all carboxyl groups react with calcium cations or at least a portion of them necessary for the precipitation of mixed humates [75]. In this case, different coagulation threshold values (according to Kukharenko [75]) at the same concentration of carboxyl groups were reported. For example, the HAs of brown coal from the Babaevskoe deposit and weathered coal from the Karagailinskoe deposit each contained 3.00 mg-equiv/g of carboxyl groups, but the coagulation thresholds for the solutions of the former and latter samples were 19 and only 5 mg-equiv of $CaCl_2/1$ per liter of humate, respectively. Opposite examples when the samples of HAs had different concentrations of carboxyl groups at the same coagulation threshold values were also described [75].

One additional fact that contradicts the concepts [50, 79] is that a large excess of an electrolyte over the content of carboxyl groups is necessary for the formation of a precipitate of mixed humates [75], and the electrolyte amount can be greater by dozens of times for different peat HA samples [9, 14, 103].

The above facts do not deny the important role of the exchange reaction of the humates of univalent cations with polyvalent ones; however, at the same time, they make it possible to assert that the exchange reaction is not a sole reason for the precipitation of mixed humates. A ratio between hydrophilic and hydrophobic fragments in the molecules of HAs exert a considerable effect: the more hydrophobic the molecules, the less the coagulation threshold value and vice versa. Therefore, the formation a mixed humate precipitate is a result of a combined effect of particle agglomera-

tion due to an exchange reaction and the salting-out action of an electrolyte. For this reason, Kukharenko [75] proposed to use the term *aggregation*, which combines the ion exchange and salting out processes, for the solutions of HAs instead of the terms *coagulation* and *precipitation.*

Two remarks should be additionally made. First, the dependence of a coagulation threshold value on a ratio between the hydrophilic and hydrophobic fragments of HA molecules is indicative of an important role of disjoining pressure in the stability of the solutions of humates, but this was not taken into account by Kukharenko [75]. Second, a decrease in the coagulation threshold value with the hydrophobicity of HAs confirms that precipitation occurs from a colloidal rather than true solution.

The term *aggregation threshold* should be considered inadequate for the following reasons: The process of aggregate formation from separate molecules occurs according to the molecules—molecular associates—molecular aggregates sequence. Because aggregates with particle sizes smaller than 10^{-4} cm occur in (colloidal) solution in spite of the presence of an interface [27, 100], it turned out that the aggregates were formed in the absence of a precipitate (approximately, as latent coagulation [27, 100] or an induction period of precipitation [4]), whereas the aggregation threshold is determined based on the onset of the formation of precipitates rather than aggregates [66, 75]. A precipitate is formed on the subsequent agglomeration of aggregates rather than on the appearance of them; because of this, they can be visually observed. Consequently, based on the appearance of a precipitate, it is impossible to establish a minimum electrolyte concentration at which the formation of microaggregates comes into play. Actually, a threshold of precipitate formation from colloidal particles rather than an aggregation threshold is determined in accordance with an accepted procedure; in connection with this, the application of the term *aggregation threshold* makes no sense.

The term *structurization threshold* is also debatable [83]. First, structurization in the solutions of humic substances can also occur without the action of electrolytes; for example, gels are formed as the concentration of humic substances is increased [40, 41, 122]. Second, the formation of structures in colloidal and microheterogeneous systems is a consequence of the coagulation of these systems [27, p. 313]. In other words, coagulation precedes structurization; that is, in these processes, coagulation is primary and structurization is secondary. As the concentration of humic substances is increased, structurization can be clearly detected by the appearance of the structural viscosity of solutions. For the aqueous and alkaline solutions of humates, the initial concentration of structurization depends on the value of pH, the type of cations, and the origin of HAs. Thus, it is 3—6% for sodium humates obtained from peat [25, 40, 41] or 9—10% for those from brown coal [122]. Note that the formation of new structural components with an interface in the solutions of humic substances under the action of electrolytes comes into play before the appearance of precipitates. Consequently, the term *structurization threshold* has the same disadvantage as the term *aggregation threshold* because a later point in time of the onset of structure formation is detected rather than the instant of the onset of coagulation. Finally, note that, generally, there are no unstructured bodies in nature: each atom, molecule, associate, or assembly has its structure. Therefore, the use of the term *structurization threshold* is inconvenient because it is always necessary to explain which particular structures are concerned.

For solving a problem of the most acceptable term, it is necessary to consider that the process of precipitation upon the introduction of polyvalent cations into a dilute alkaline solution of sodium (potassium, ammonium) humates occurs at least in two steps. The first step is the transformation of a true solution into a colloidal one by joining many humate molecules through metal bridges or hydrogen bonds as a result of an exchange reaction of univalent cations for polyvalent cations. By selecting concentrations, it is possible to obtain a colloidal solution of mixed humates, for example, of calcium and sodium, with an interface between the microaggregates (micelles) of these humates and a dispersion medium (an alkali solution). Upon the subsequent introduction of new electrolyte portions, the second step—the precipitation of the mixed humates from colloidal solution—comes into play. If an acid rather than a salt of a polyvalent cation is added to the solution of sodium humates, colloidal particles are formed at the first step due to the agglomeration of the molecular associates of HAs to microaggregates at hydrogen bonds.

Upon the introduction of sodium chloride into a solution of humates, a colloidal solution is initially formed from the alkaline or neutral solution as a result of the displacement of humates from the dispersion medium by the mechanism of salting out and particle agglomeration on the interaction of the hydrophobic fragments of different HA macromolecules, and only then precipitation occurs.

Regardless of which of the above three mechanisms describes the conversion of the true alkaline solutions of humates into colloidal solutions, at the second stage, the adhesion of colloidal particles with the formation of a sediment occurs in all cases upon the further introduction of an electrolyte; that is, the sediment of HAs is formed from a colloidal rather than

true solution. Thus, the observed phenomenon of the precipitation of humic substances by electrolytes from aqueous alkali solutions is of colloid-chemical nature. Therefore, for the characterization of this process, it is most correct to use the term *coagulation*, which is conventional in colloid chemistry, and the smallest electrolyte amount at which a sediment is formed from colloidal solution should be characterized by the term *coagulation threshold*.

CHEMISTRY OF HUMIC ACIDS AND THEIR COAGULATION THRESHOLDS

The practical use of data on coagulation threshold values is based on their dependence on a ratio between hydrophilic and hydrophobic fragments in the molecules of HAs [66, 75]. Polar oxygen- and nitrogen-containing functional groups (alcohol, phenol, carboxyl, carbonyl, ether, amino, etc., groups) possess hydrophilic properties, whereas condensed aromatic fragments possess hydrophobic properties. The coagulation threshold values of HAs clearly change in the genetic order of fossil solid fuels at different stages of metamorphism: peat—earthy brown coal—bright brown coal—weathered coal [71—76]. In this order of peat HAs, the genetically youngest species have the smallest degree of condensation of polyconjugation systems and the greatest amounts of aliphatic chains, ether bonds, and functional groups; therefore, they are most hydrophilic and most resistant to coagulation. At the stage of the formation of brown coal, the degree of condensation of aromatic nuclei in the molecules of HAs increases and the fraction of side chains, ether bonds, and functional groups decreases; therefore, the coagulation threshold value decreases. For the HAs extracted from different types of humified raw materials, the following coagulation threshold values were obtained (in mg-equiv of $BaCl_2$ per liter of humate): sapropel, 36—107; peat, 26.2—31.2; earthy brown coal, 22.0; bright brown coal, 12.2; and weathered coal, 9.6 [9, 14, 72—74, 101, 103]. These characteristic properties are expressed so that it is possible to easily distinguish the HAs of peat from the HAs of other higher rank solid fuels [71, p. 131].

The coagulation threshold value of HAs also clearly decreased with the degree of peat decomposition [9, 14, 83, 103]; in this case, it turned out that, at the same degree of decomposition, the coagulation threshold of the HAs in lowland peat is higher than that of high-moor peat. This can be explained by the fact that the high-moor peat is formed under the conditions of an acidic medium during the millennia; in this time, the hydrolytic cleavage of a portion of side chains with polar groups from the molecules of HAs occurred; therefore, the hydrophobicity of the HA molecules of high-moor peat is higher than that of lowland peat. However, the HAs of sapropel are even more hydrophilic than the HAs of peat; therefore, their coagulation threshold is higher than that in the HAs of peat by a factor of 2—4 [101]. This is related to the special conditions of the formation of sapropel, namely, the low oxygen content of lake water, which hampers the cleavage of hydrophilic side chains in HAs under the action of the enzymatic apparatus of microorganisms and abiotic oxidation.

For different genetic types of soils (sod-podzol soil, chernozem, red soil, etc.), a relationship of the coagulation threshold value with the molecular structure of HAs was also established: the smallest coagulation thresholds are observed in the solutions of HAs from chernozem soils because their molecules contain the greatest amount of hydrophobic aromatic fragments and the smallest amount of hydrophilic side chains, as compared with those in the HAs of sod-podzol and other types of soils [2, 66, 93, 133].

The coagulation threshold value is sensitive to the molecular structure, so that different fractions of HAs separated from a sample essentially differ from each other. For example, the fractions of peat HAs have the following coagulation thresholds: a pyrophosphate fraction, 8—10 mg-equiv of $BaCl_2$ per liter of humate; a fraction additionally separated with a 0.1 M sodium hydroxide solution at 18—22°C, 14—16; and a fraction additionally extracted with a 0.02 M sodium hydroxide solution at 80°C, 26—30 [9]. The fractions of peat HAs isolated with different alkaline extractants and acetone—water mixtures are also essentially different in terms of coagulation thresholds [14].

In a number of chemical technologies, the coagulation threshold value is of crucial importance for the selection of raw materials for the manufacture of humic preparations for different practical applications. For example, HAs with a low coagulation threshold (smaller than 10 mg-equiv of metal per liter of sodium humate) are better suitable for the removal of heavy metal impurities from water. Upon the introduction of minimum amounts of the alkaline solutions of such HAs into water to be purified, heavy metals are precipitated in the form of mixed humates and complexes [23, 33, 42—45, 57, 58, 62, 77, 81, 91, 98, 99, 113, 115, 116, 124]. These HAs can be obtained from brown coal. On the contrary, if the ions of metals should be retained in solutions, for example, in technologies for the production of biologically active liquid trace-element fertilizers (Zn, Mn, Cu, etc.), it is better to take humic preparations with higher coagulation thresholds (30—50 mg-equiv of M or more per liter of sodium humate), which can be obtained from peat or sapropel.

Thus, the coagulation threshold value can be a tool for a comparative study of the properties of HAs of different genesis and their individual fractions. For the same sample, the coagulation threshold depends on the concentration of HAs, the value of pH, and the types of cations and anions; therefore, the experimental conditions should be constant in order to obtain comparable results. A united standard procedure for the determination of the coagulation threshold of humic substances is currently unavailable. For its development, it is necessary to substantiate the forms and concentrations of cations and anions, the concentrations of the solutions of humic substances, the methods of the introduction of reagents, the duration of an experiment, and the methods of the detection of the eventual result. There is no doubt that this procedure is required, and it would be most reasonable to develop it under the aegis of the International Peat Society or the International Humic Substances Society.

CONCLUSIONS

The precipitation of humic substances from the aqueous and alkaline solutions by electrolytes is widely used in chemical technologies for the processing of peat, brown coal, black coal, sapropel, and other humified materials and in the technologies of water preparation, well drilling, metal ore leaching, etc. The precipitation processes of humic substances occur under natural conditions on a global scale, and they are responsible for the formation of many metallic ore deposits, the incursion of land into the ocean with the formation of extensive river deltas, the formation of agriculturally valuable soil structures, etc.

The precipitation of humic substances by electrolytes from aqueous and alkaline solutions occurs in two stages: first, the transformation of true solutions into colloidal ones and, second, a decrease in the aggregative stability, the adhesion of particles, and the formation of sediments. At the first stage, the mechanisms of conversion of true solutions into colloidal solutions differ depending on the value of pH: in an acidic medium, initially, associates are formed from several molecules of humic substances due to hydrogen bonds followed by the formation of microaggregates (micelles) with and interface; in alkaline and neutral media, the formation of microaggregates occurs due to the association of many molecules through the bridges of polyvalent cations (Ca^{2+}, Ba^{2+}, Fe^{3+}, etc.). On the salting out of humic substances from true solutions, colloidal particles are formed due to the displacement of separate molecules from the dispersion medium; then, supramolecular structures with an interface—micelles or microaggregates of colloidal sizes—are formed upon the contact of mole-cules at hydrophobic sections. The colloidal solutions of humic substances are thermodynamically unstable; therefore, the agglomeration and sedimentation of their particles occurs at the second stage.

The formation of the sediments of humic substances is of colloid-chemical nature; therefore, the term *coagulation*, which is conventional in colloid chemistry, is most suitable for the characterization of the above processes.

The coagulation thresholds of the HAs of solid fuels are very typical for different stages of metamorphism, and they adequately reflect the nature of fossil fuels and the genetic features of HAs obtained from other humified materials, such as sapropel, soil, and biohumus.

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