

TECHNICAL REPORT 89-08E

THE COORDINATION CHEMISTRY OF HUMIC SUBSTANCES

R. GRAUER

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PSI, Würenlingen and Villigen

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ABSTRACT

Dissolved humic substances are ligands which can influence the speciation of certain radionuclides in natural waters. It is therefore necessary to take account of this phenomenon in repository safety assessment model calculations.

In operational terms, dissolved humic substances can be sub-divided into humic and fulvic acids, both groups being polyfunctional macromolecules with a large structural variety. Description of their solution chemistry is restricted to very simple models due to the inhomogeneity of their properties.

The protolytic behaviour of humic substances is determined mainly by carboxyl- and phenolic OH-groups whose acidities are modified by substituents. A model which assumes a normal distribution of the pK_a values for both acid groups would appear to have a good chemical foundation.

There are, however, no chemically realistic models available which give a basic description of the wide range of complexation properties of humic substances with dissolved metals. All the models make drastic simplifications and, although capable of reproducing experimental data, do not allow any extrapolation to concentration ranges outwith those covered by the experiments.

By way of a minimum description, the humate complexes can be treated as a mixture of two to three single complexes with 1:1 stoichiometry. The stability constants and the concentrations of the individual ligands are then adjustable parameters which are dependent on the concentration conditions selected and are valid only for specific pH-values and ionic strengths. As there is no simple model for describing the pH-dependence of complexation, most of the literature data (generally determined for low pH-values) are not in fact applicable in the case of natural waters.

Humic substances affect not only the solution chemistry of the metals but also their sorption on minerals. The mineral surfaces are modified through adsorption of organic material, which in turn alters their sorption properties. These processes are understood in qualitative terms.

As it is unlikely that a comprehensive predictive model of complexation by humic substances will be available in the foreseeable future, it is suggested that experiments providing an empirical description of metal/humic substance interactions using realistic pH-values and metal/ligand ratios be carried out. Besides parameter studies and experiments in synthetic or formation waters, analogue studies could also prove useful.

ZUSAMMENFASSUNG

Die gelösten Huminstoffe stellen Liganden dar, die die Kationen-Spezifizierung in natürlichen Wässern beeinflussen, und es besteht das Bedürfnis, diesen Einfluss in Modellrechnungen zu berücksichtigen.

Die gelösten Huminstoffe werden operationell in Humin- und Fulvinsäuren unterteilt. Beide Gruppen sind polyfunktionelle Makromolekeln mit einer grossen strukturellen Vielfalt. Weil sie keine einheitlichen Stoffe darstellen, ist die Beschreibung ihres lösungsschemischen Verhaltens nur mit Hilfe stark vereinfachender Modelle möglich.

Das Protolyseverhalten der Huminstoffe wird vorwiegend durch Carboxyl- und phenolische OH-Gruppen bestimmt, deren Acidität durch Substituenteneinflüsse modifiziert wird. Elegant und chemisch gut begründet erscheint ein Modell, das für die beiden sauren Gruppen je von einer Normalverteilung der pK_a -Werte ausgeht.

Es bestehen aber keine Modelle, die das vielfältige Ligandenverhalten der Huminstoffe im Einklang mit der chemischen Realität elementar beschreiben. Alle Modelle vereinfachen so stark, dass sie wohl in der Lage sind, experimentelle Daten zu reproduzieren, aber keine Extrapolation auf experimentell nicht abgedeckte Konzentrationsbereiche erlauben.

Im Sinne einer Minimalbeschreibung lassen sich die Humatkomplexe als eine Mischung von zwei bis drei Einzelkomplexen mit 1:1-Stöchiometrie behandeln. Dabei sind die Stabilitätskonstanten und die Konzentrationen der Einzelliganden adjustierbare Parameter, die von den gewählten Konzentrationsverhältnissen abhängen. Sie gelten ausserdem nur für bestimmte pH-Werte und Ionenstärken. Weil kein einfaches Modell zur Verfügung steht, das die pH-Abhängigkeit der Komplexbildung beschreibt, lassen sich die meist bei tiefen pH-Werten ermittelten Literaturdaten auch nicht approximativ auf natürliche Wässer übertragen.

Die Huminstoffe beeinflussen nicht nur die Lösungschemie der Metalle, sondern auch ihr Sorptionsverhalten an Mineralien. Die mineralischen Oberflächen werden durch die Adsorption von organischem Material modifiziert und weisen nun ein verändertes Sorptionsverhalten auf. Diese Vorgänge werden qualitativ verstanden.

Weil in absehbarer Zeit kein umfassendes prädiktives Modell der Komplexbildung durch Huminstoffe zur Verfügung stehen wird, werden Experimente vorgeschlagen, welche die Metall/Huminstoff-Wechselwirkung bei realistischen pH-Werten und Metall/Ligand-Verhältnissen empirisch beschreiben. Neben Parameterstudien und Experimenten in Modell- oder Standortwässern dürften auch Analogstudien hilfreich sein.

RÉSUMÉ

Les humines dissoutes représentent des ligands qui influencent la spéciation des cations dans les eaux naturelles. Les calculs sur modèle doivent tenir compte de cette influence.

Opérationnellement, les humines dissoutes sont subdivisées en acides humiques et fulviques. Ces deux groupes sont des macro-molécules polyfonctionnelles d'une grande diversité structurale. Vu qu'elles ne représentent pas de substances homogènes, on ne peut décrire leur comportement chimique en solution qu'à l'aide de modèles simplifiés à l'extrême.

Le comportement de protolyse des humines est essentiellement déterminé par des groupes de carboxyles et d'hydroxyles phénoliques, dont l'acidité est modifiée par l'influence de substituants. Un modèle partant chaque fois, pour les deux groupes acides, d'une répartition normale des valeurs pK_a apparaît comme étant chimiquement bien fondé.

Mais il n'existe pas de modèles donnant une description - élémentaire et en harmonie avec la réalité chimique - du comportement de ligands variés des humines. Tous les modèles procèdent à de si fortes simplifications qu'ils sont tout à fait en mesure de reproduire des données expérimentales, mais ne permettent pas d'extrapolation à des domaines de concentration que l'expérience ne couvre pas.

Dans le sens d'une description minimale, on peut traiter les complexes humiques comme le mélange de deux à trois complexes individuels, avec stoechiométrie 1:1. Les constantes de stabilité et les concentrations des ligands individuels sont des paramètres ajustables, dépendant des concentrations choisies. Elles ne s'appliquent en outre que pour certaines valeurs pH et forces ioniques. Vu que l'on ne dispose pas d'un modèle simple décrivant la dépendance du pH de la complexation, on ne peut pas appliquer - même approximativement - les données de la littérature, obtenues pour la plupart pour des pH bas, aux eaux naturelles.

Les humines influencent non seulement le comportement chimique des métaux en solution, mais aussi leur comportement de sorption sur les minéraux. Les surfaces minérales sont modifiées par l'adsorption de matériel organique et présentent alors un comportement de sorption différent. Ces processus sont compris qualitativement.

L'avenir proche ne livrera pas de modèle prévisionnel de la complexation par les humines, et l'on propose donc des expériences qui décrivent empiriquement l'interaction métal/humine pour les valeurs pH et des rapports métal/ligand réalistes. Outre les études de paramètres et les expériences dans les eaux de modèle et de site, des études d'analogie devraient aussi s'avérer utiles.

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1. INTRODUCTION

In addition to inorganic ligands, natural waters generally contain organic compounds in concentrations which can significantly influence the speciation of trace metals. In soft waters, the contribution of these substances to alkalinity should not be ignored. For these reasons, the organic components in water have been receiving increasing attention in the geochemical literature over the past 20 years and their importance has been highlighted in a number of review articles /56, 75, 99, 101/.

A small fraction of the aquatic organic substances are present as identifiable, low molecular weight compounds and, in principle, their contribution to the complexation of metal ions can be estimated. The situation is somewhat different in the case of macromolecular humic substances, since these have diverse structures of which often only the main features are known. Their complexation behaviour can only be described by making more or less arbitrary assumptions using formal stability constants which can at best be applied only in exceptional cases to the conditions in natural waters.

Humic substances are omnipresent and occur in particularly large quantities in sedimentary rocks. Their influence on the mobility of radionuclides therefore has to be taken into consideration in repository safety analyses. This is virtually impossible given the present level of knowledge on the subject and this report does not claim to offer a solution to the dilemma.

The emphasis of this report lies rather on a discussion of models used to investigate the protolytic and ligand behaviour of humic substances, the aim being to achieve a basic understanding of the limits of such models and to prevent, amongst other things, the careless use of literature data in model calculations.

The literature on humic substances is very extensive. Selection of cited works is therefore somewhat arbitrary and it may be that important publications have been overlooked. A number of books are available which give detailed information on humic substances and their chemistry and these were consulted during the writing of this report.

The book by THURMAN /118/ deals with natural and anthropogenic aquatic organic substances. It contains a wealth of information on the concentrations and origins of the individual types of compound. Of the numerous monographs available on humic substances, the textbook by STEVENSON /110/ is considered to be most suitable as an introduction to the topic. The book by AIKEN et al. /1/ deals comprehensively with the geochemistry, isolation and characterisation of humic substances and contains around 1200 literature references. In /28/, the emphasis is more on structural characterisation and complexation. The book by RASHID /98/ concentrates mainly on marine humic substances - both dissolved and in sediments. Unfortunately, a recent publication on the role of humic substances in the environment /41/ was not available at the time of writing this report.

The numerous aspects of complexation with simple ligands, humic substances and inorganic colloids in natural waters are discussed in detail by BUFFLE /17/, while the book by KRAMER and DUJNKER /64/ contains essays on metal complexes with humic substances.

Finally, reference is made to two articles appearing in "handbooks" /26, 58/ which deal with humic substance complexes of the actinides. The "grey" literature on this topic is summarised in /10/ and /39/.

2. HUMIC SUBSTANCES

2.1 The operational definition of humic substances

Humic substances are macromolecules with complex structures which were first isolated from soils and later from natural waters. The complex nature of their structure meant that, for a long time, they could only be characterised very roughly and, even today, the identification process is still linked closely with the isolation and separation techniques used. Figure 1 shows the procedure for fractionation of humic substances from soils /110/. The starting material is first washed with 0.1 M hydrochloric acid, which also separates out low molecular weight organic materials. In the next step, the material is extracted with 0.5 M sodium hydroxide solution and the undissolved component is defined as humin. Acidification of the solution to pH 1 leads to partial precipitation of the organic material. The precipitated products are the humic acids, while those remaining in solution are termed fulvic acids. A further separation into gray and brown humic acids and into hymatomelanic acids is not always undertaken. The separation into gray and brown humic acids can also be made on the basis of electrophoretic mobility, the brown component being more mobile.

The term "kerogen" is used in connection with fossil sediments. It is generally understood to mean the insoluble organic substance, but sometimes also the sum of humin, humic and fulvic acids.

Humic substances form the main component of dissolved organic carbon in waters (Fig. 2). The working definition for aquatic humic substances is different to that for humic substances originating from soils /118/. According to this definition, humic and fulvic acids are the coloured macromolecular polyelectrolytes which, following acidification to pH 2, are adsorbed on non-ionic resins (e.g. poly-methylmethacrylate, XAD-resins). Because of this tendency, they are also termed hydrophobic substances. In this separation process, the coloured fraction remaining in solution is termed hydrophilic acid and has to be isolated using a special procedure. Little is known at present about the nature of this class of substance. Presumably it has a lower molecular weight than the fulvic acids and contains more carboxyl groups per carbon atom /71/. The hydrophilic acids probably contain saccharic acids (aldonic, uronic and polyuronic acids) /118/. Polyuronic acids also occur in the humus of the soil but are extracted together with the humic and fulvic acids /50/.

The methods for isolating and fractionating humic substances will not be discussed in greater detail here. Chapters 13 to 16 in /1/ and /82/ provide information on the state-of-the-art regarding these techniques.

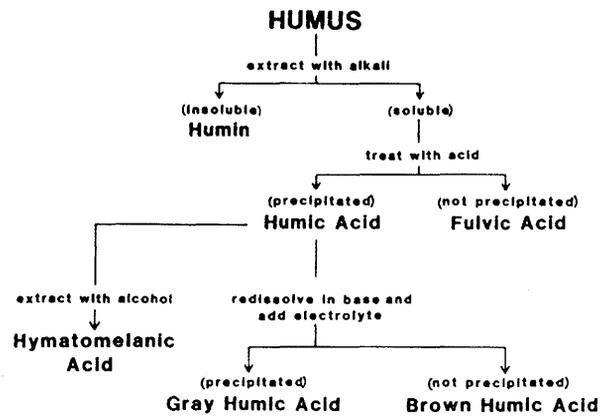


Figure 1: Scheme for fractionation of humic substances from soils /110/

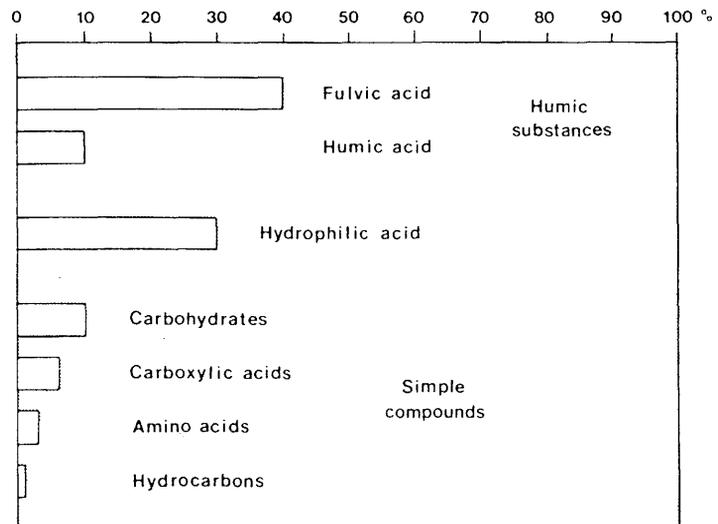


Figure 2: Histogram of dissolved organic carbon (DOC) for an average river-water with a DOC content of 5 mg/litre /118/

2.2 Molecular weight and composition of humic substances

The mean molecular weight of humic substances is determined inter alia by small-angle X-ray scattering, gel chromatography, ultrafiltration and vapour pressure osmometry /110, 118/. The values obtained depend in each case on the method used.

The molecular weights of fulvic acids from waters and soils lie in the range 500 to 2000 daltons (D) /118/ and they therefore form true solutions. However, fulvic acids with 5000 to 10,000 D are also found /119/. Fulvic acids with 500 to 1000 D seem to be relatively monodispersed /2/.

Aquatic humic acids have higher molecular weights than fulvic acids (2000 to 5000 D) and their particle sizes are larger than 1 nm. They can therefore be classified as colloids /118/. Humic acids from soils with molecular weights of up to 50,000 to 100,000 D /110/ are clearly colloidally dispersed.

Humic substances are characterised by a high oxygen content, which is higher for fulvic acids than for humic acids. The elemental composition depends to a large extent on the origin and genesis of the compounds. Table 1 gives the ranges of the elemental contents.

Table 1: Elemental content (in percent) of fulvic and humic acids (dry, ash-free) /110/

Element	Fulvic acids	Humic acids
C	40-50	50-60
O	44-50	30-35
H	4-6	4-6
N	<1-3	2-6
S	0-2	0-2

It can be seen from this Table that nitrogen and sulphur are of secondary importance as ligand atoms. With nitrogen contents of about 1 %, fulvic acids with molecular weights below 1400 D contain less than one nitrogen atom per molecule.

The functional group content is of interest from the point of view of the protolytic and ligand behaviour of humic substances. These are mainly carboxyl and phenolic OH-groups. In this case, the values measured are also dependent on the particular method selected for the investigation /118, 92/. The most reliable values seem to be those for the carboxyl groups, for which an average content of 5 - 6 mmol/g can be assumed (Table 2). Typical values for the phenolic OH-groups are around 1 to 3 mmol/g. In general, the carboxyl content of fulvic acids is slightly higher than that of humic acids from the same location /118/; this rule does not apply for the phenolic OH-groups.

Table 2: The contents of acidic functional groups of humic and fulvic acids. After /17, 68, 118/.

	Carboxyl groups (mmol/g)	Phenolic OH groups (mmol/g)	Total acidity (mmol/g)
<u>Fulvic Acids</u>			
Origin:			
Soil	6.1-11.2 $\bar{x} = 8.2$	1.2-5.7 $\bar{x} = 3.0$	6.4-14.2 $\bar{x} = 10.3$
Soil	6	3.0	
Water	6.5-10.7	1.0-4.7	9.6-16.6
Water	6	2.0	
Groundwater	5.1-5.5	1.6	
Lakes	5.5	0.5	
Rivers	5.5-6.0	1.5	
Moors. Wetlands	5.0-5.5	2.5	
Sea-water	4.4-8.9	0.9-3.6	
<u>Humic Acids</u>			
Origin:			
Soil	1.5-5.7 $\bar{x} = 3.6$	2.1-5.7 $\bar{x} = 3.9$	5.6-8.9 $\bar{x} = 6.7$
Sediments	1.8-3.9	0.9-1.9	
Water	4.5-5.9	2.2-3.7	7.1-8.9
Rivers	4.0-4.5	2.0	
Moors. Wetlands	4.0-4.5	2.5	

Since the steric arrangement of the functional groups is important for complexation behaviour, it is of interest to have information on the aromatic carbon component. In the case of marine humic substances this amounts to 10 to 15 % /118/, but it can also be completely absent /49/. In substances from rivers and soils, the figure is between 20 to 40 and 22 to 35 % respectively /118/. Humic and fulvic acids with the same origin can differ markedly. In one river, the aromatic carbon content of the fulvic acid is 17 % while that of the humic acid is 30 % /71/.

The lower carboxyl content of humic acids, together with the fact that their molecular weight is high compared to that of fulvic acids, results in a reduced solubility of humic acids. Natural waters therefore contain 5 to 25 times more fulvic acids than humic acids /118/.

Only limited information is available concerning the quinone contents of humic substances; these are important for redox behaviour and fluctuate between 0.7 and 2.1 meq/g /68/.

2.3 Structural models of humic substances

A whole series of different chemical and physical methods has to be employed for the structural characterisation of humic substances. Apart from degradation reactions, these consist mainly of infrared- and C-13 nuclear magnetic resonance spectroscopy. Reviews of the different methods and their efficiency are given, for example, in /1, 28, 127/. One has to be aware of the fact that each structural model is the result of a complex combination process and should therefore be understood as a prototype rather than as a true picture of reality. Worthy of comment are the efforts towards generating structural models of humic substances using a computer program /84/.

Numerous suggestions as to the structure of humic substances have been published in the literature. The selection given in Figures 3 to 8 speaks for itself. One model is based on intermolecular interactions (Fig. 5). Kleinhempel's model (Fig. 8) is impressive in that it gives an indication of the extremely complex links between different structural elements.

The models show that the humic substances with a high aromatic component contain numerous bidentate ligands. Structures 3 to 5 suggest that when several isolated carboxyl groups are present, pseudochelates can be formed.

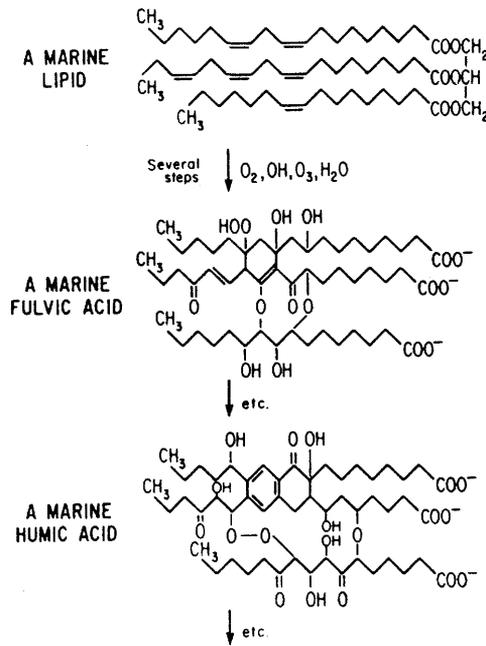


Figure 3: Representative structures in the dynamic continuum of formation of humic acids from lipids /49/

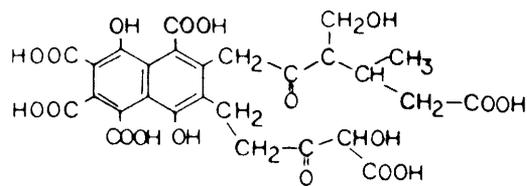


Figure 4: Proposed structure for a low molecular weight fulvic acid. J. BUFFLE, after /111/

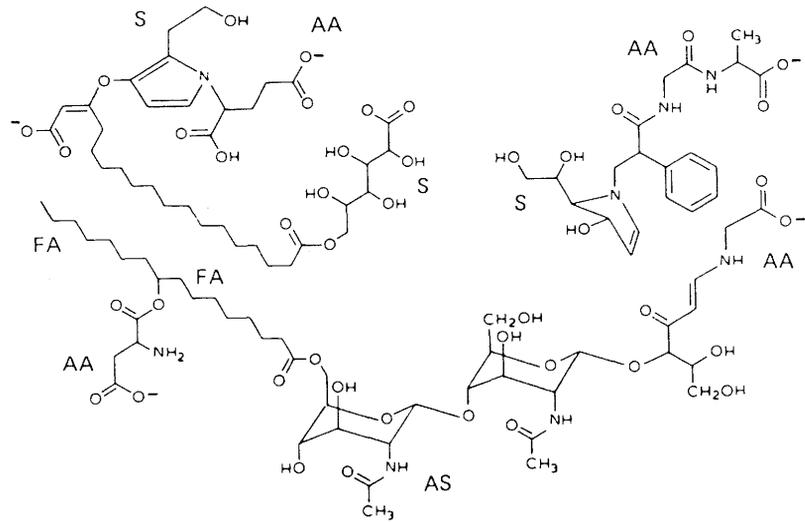


Figure 5: Proposed structure for marine humic substances. AA: amino acid; FA: fatty acid; S: sugar; AS: amino sugar /14/

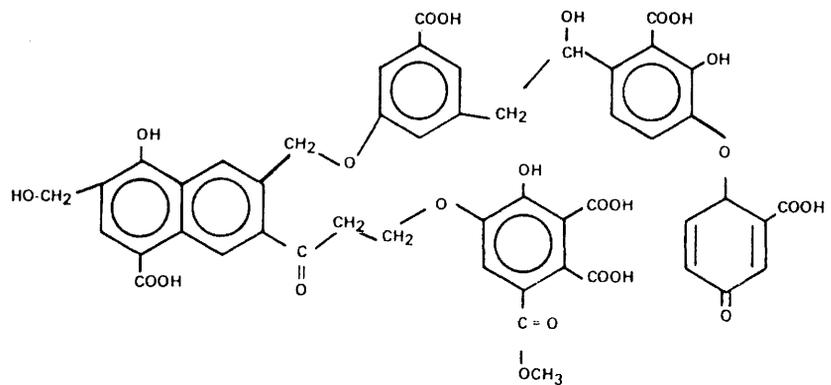


Figure 6: Speculative model of a humic acid with high aromatic content /67/

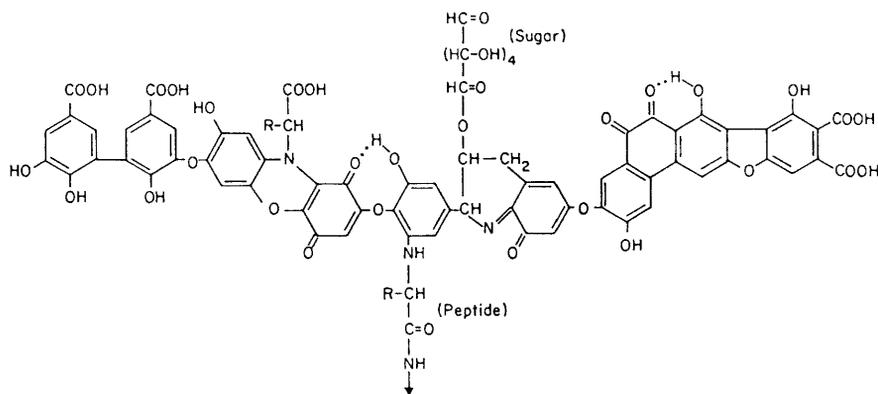


Figure 7: Hypothetical structure of humic acid according to STEVENSON /110/

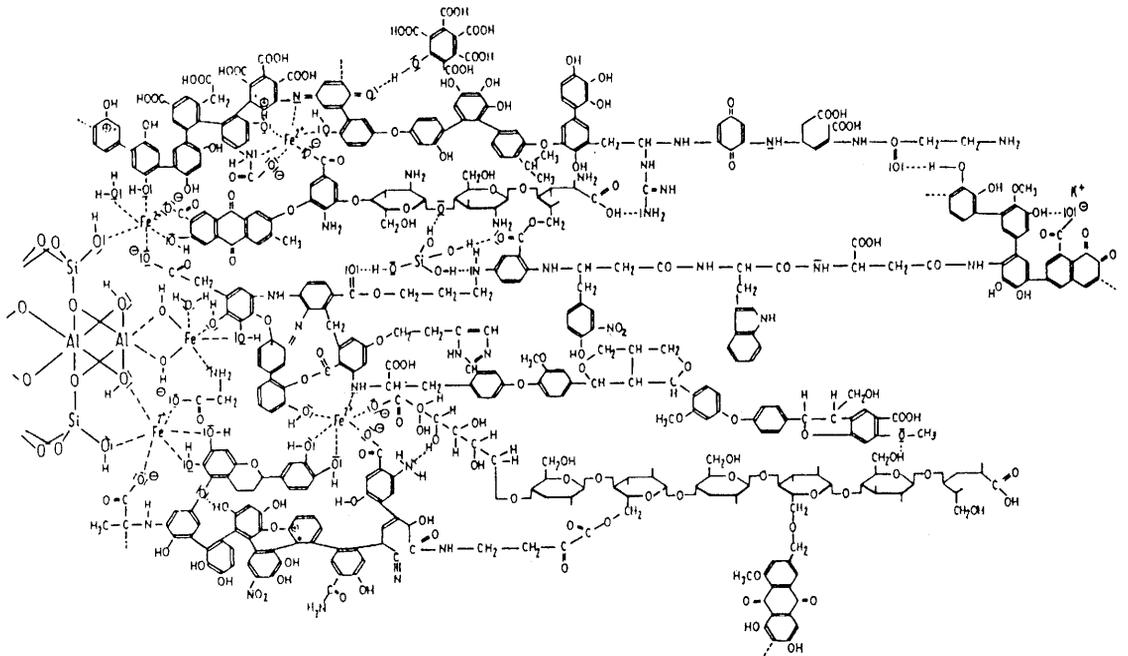


Figure 8: Structure proposed by KLEINHEMPEL for a high molecular weight humic acid (around 13,000 daltons), after /17/

2.4 The formation of humic substances

The chemical and microbiological processes which lead to the formation of humic substances have never been explained in detail. An expert judges this field to be "one of the least understood aspects of humus chemistry and one of the most intriguing" (/110/, p. 195).

At least four general concepts exist for the formation of humic substances in soils:

- a) Humic substances originate from the partial microbial degradation of lignin (Fig. 9). The aliphatic side-chains are oxidised to carboxyl groups, the methoxyl groups are decomposed and phenols are formed through biochemical reactions. According to this model, fulvic acids would be formed from the humic acids via fragmentation and oxidation processes.

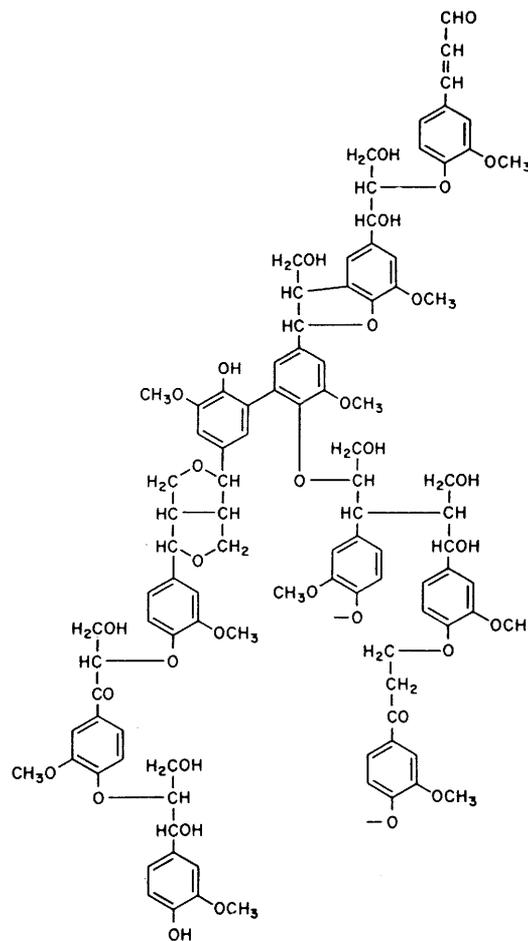


Figure 9: The structure of lignin /98/.

- b) A second model assumes that lignin is decomposed by microorganisms into phenolic aldehydes and acids which are further oxidised enzymatically to quinones. These materials finally polymerise into humic substances.
- c) In this case, the more readily degradable cellulose (Fig. 10) is assumed as the starting material rather than lignin. The degradation products are polyphenols, which are again oxidised enzymatically and finally polymerise.

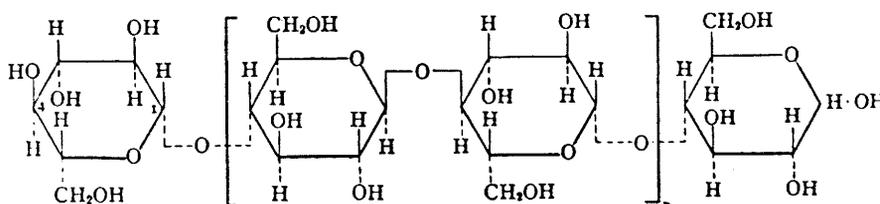


Figure 10: The structure of cellulose.

- d) In the sugar-amine condensation model, it is assumed that reducing sugars condense together with amino acids to form humic substances. These starting materials are produced by microbial degradation of cellulose and polypeptides.

According to STEVENSON /110, 111/, the lignin degradation model a) is now out of date. Models b) and c) seem to be most relevant. The low nitrogen contents of humic substances are difficult to reconcile with model d).

Aquatic humic substances can be washed in from the land or formed through the decay of aquatic vegetation. In lakes and in the sea, the metabolic and degradation products of algae form the main source for the synthesis of humic substances (Fig. 11) /54, 118, 126/. This source of "raw material" also accounts for the strongly aliphatic character of aquatic humic and fulvic acids. For similar reasons, the humin and kerogen in marine sediments are also predominantly aliphatic /50/.

Humic substances can therefore be formed from a very wide range of raw materials and the number of possible combinations is astronomically high. It is therefore relatively easy to appreciate that the structure of humic substances will depend on location and that, even at a single location, they will not have a uniform composition.

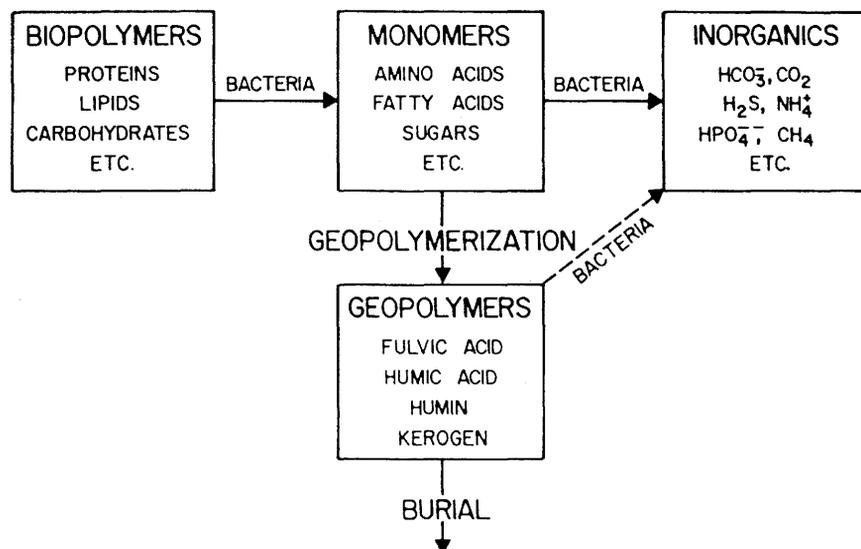


Figure 11: Idealised scheme for transformation of organic matter in sediments during early diagenesis /7/

2.5 The diagenesis of humic substances

Following deposition in sediments, humic substances undergo further chemical and biological changes. However, the microbiological influence decreases rapidly with depth, the bacterial concentration already dropping dramatically in the upper sediment layers /100, 123/ (Fig. 12 and Table 3). RASHID /98/ therefore comes to the conclusion that microbiologically induced changes play a negligible role during diagenesis.

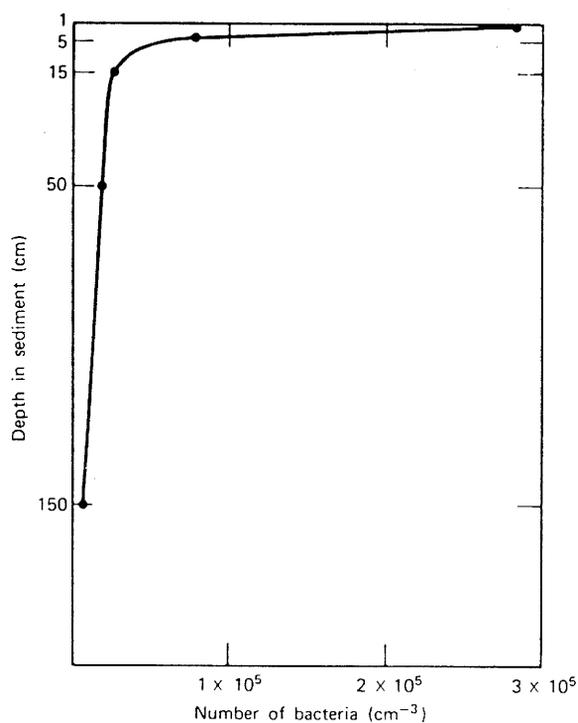


Figure 12: Profile of bacterial concentration as a function of depth in sediments from the Persian Gulf /100/.

Table 3: Bacterial contents of recent sediments (San Diego Bay, California) /98/.

Depth (cm)	Anaerobic bacteria per g sediment	Aerobic bacteria per g sediment
0-3	1.160.000	74.000.000
4-6	14.000	314.000
14-16	8.900	56.000
24-26	3.100	10.400
44-46	5.700	28.100
66-68	2.300	4.200

During diagenesis, low molecular weight fragments and inorganic end-products are produced as well as larger macromolecules /110, 111/. For terrestrial humic substances, the general diagenetic trend is presented in Figures 13 and 14. The main feature is that the carboxyl group content decreases, which means that the capacity for complexation reduces with time. The differing diagenetic evolution of biopolymers in marine and non-marine sediments is shown schematically in Figure 15.

Because of increasing condensation and the loss of polar groups, the proportion of extractable humic substances decreases as the sediments become older (Fig. 16). In the Lower Quaternary, about 20 % of the total carbon content is present in the form of extractable humic substances, but in the Middle Tertiary this figure drops to 5 %. In two shale formations of the Eocene, with total carbon contents of up to 30 %, humic acid contents of 0.4 and 6 % of the TOC were measured /54/. This trend is also recognisable in peat /126/ and in young sediments /54/.

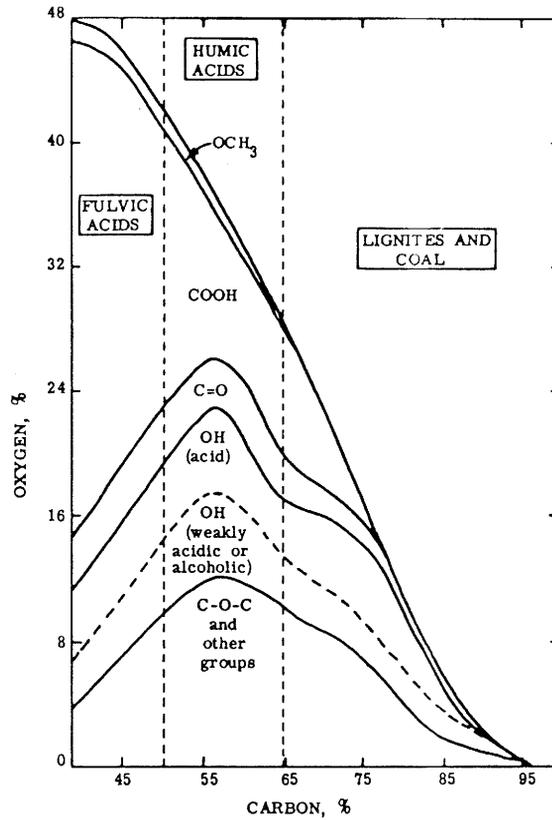


Figure 13: Proportions of oxygen-containing functional groups of fulvic and humic acids, lignites and coal /110/

Statements as to the rate of diagenetic reactions are inherently difficult to make /7/. In old sediments, however, a constant situation can be expected over long periods of time. A half-life in the order of 400,000 years has been ascertained for the decomposition of lignin in lacustrine sediments /55/.

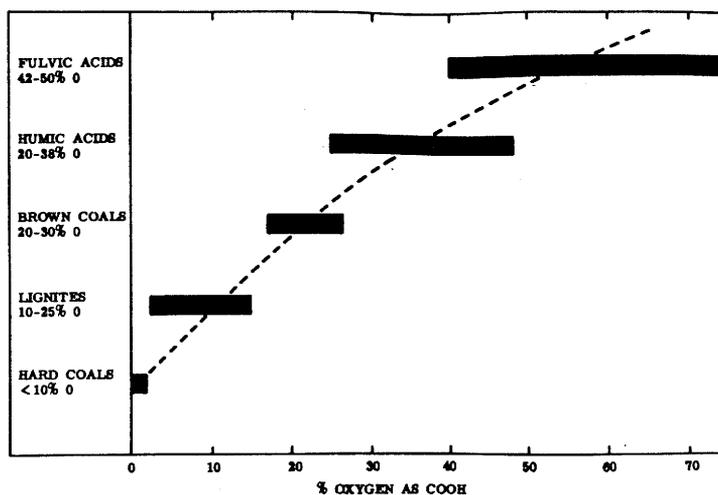


Figure 14: Variation in the proportion of carboxyl groups as a percentage of oxygen content for humic substances and coals /110/.

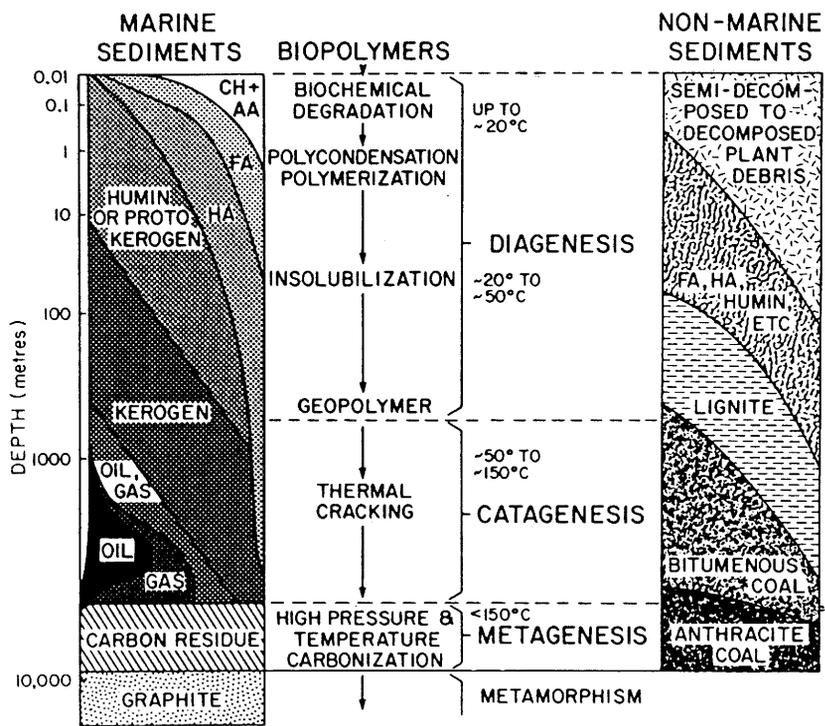


Figure 15: Generalised overview of genetic transformation of organic matter in marine and non-marine sediments. AA: amino acids; CH: carbohydrates; FA: fulvic acids; HA: humic acids /98/.

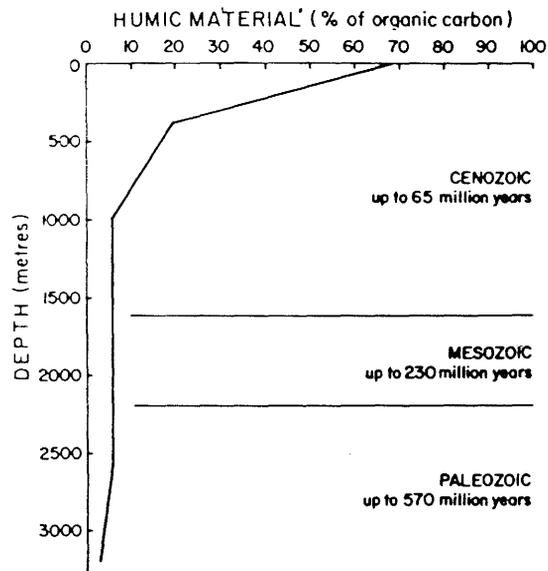


Figure 16: The percentage of humic substances in the organic component of sediments as a function of depth /98/.

2.6 The humic substance contents in waters and sediments

THURMAN /118/ gives a summary of the contents of humic substances in natural waters (Table 4). Fig. 17 shows the proportion of humic substances as a percentage of dissolved organic carbon. It is interesting to note that the content of the less well-known hydrophilic acid group can exceed that of humic substances.

Table 4: Concentrations of humic substances in natural waters /118/

Water type	Concentration (mgC/litre)
Groundwater	0.03-0.10
Sea-water	0.06-0.60
Lakes	0.5-4.0
Rivers	0.5-4.0
Wetlands	10-30

The concentrations of humic substances in deep granitic groundwaters can also be considerable. Swedish investigations indicate that the figure is in the range of 0.2 to 3.4 ppm /90/. Fractionation of these humic substances has shown that they consist almost exclusively of fulvic acids. Around two-thirds of these humic substances have molecular weights below 1000 D /4/.

In old marine sediments, the proportion of organic matter can be as high as 10 % /126/, but insoluble humin still dominates (Fig. 18) and is active in determining the sorption properties of the sediments. Mobilisable humic and fulvic acids are found only in small quantities.

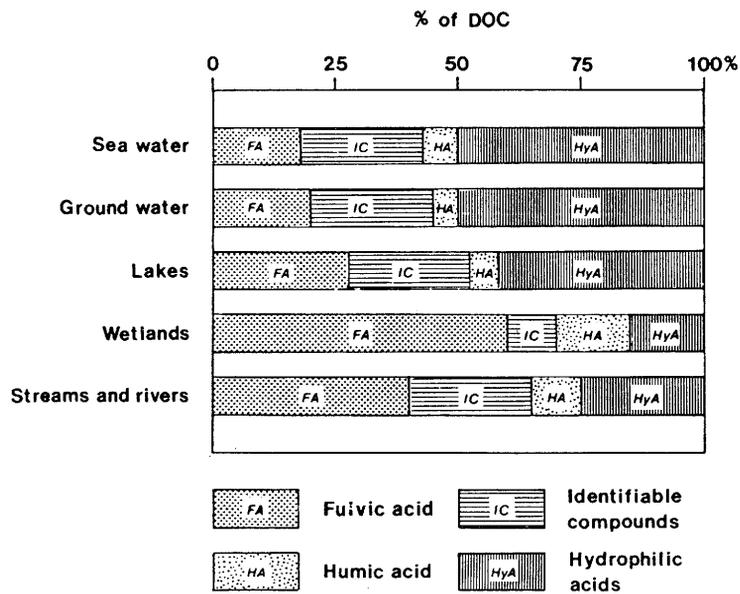


Figure 17: Distribution of humic substances and identifiable organic compounds in natural waters /118/

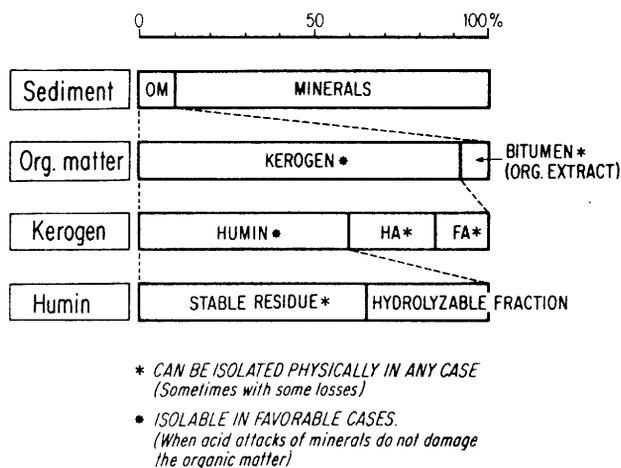


Figure 18: Composition of the organic fraction in sediments /126/

According to another source /54/, the organic carbon content of lacustrine sediments lies between 2 and 4 %. The division into individual fractions is given in Table 5.

The Belgian Boom Clay contains around 2.2 % of humic substances /6/. The dissolved carbon in the pore-water reaches values of up to 200 ppm /39/.

Table 5: Abundance of humic substances in the sediments of Japanese lakes /54/. TOC: total organic carbon. Lipids: soluble in organic solvents

Carbon	mg/g sediment	44.2±8.0
Nitrogen	mg/g sediment	4.0±0.7
Lipids	% of TOC	5.8±1.0
Fulvic acids	%	25±5.0
Humic acids	%	22±6.0
Humin	%	47±3.0

3. THE PROTOLYTIC BEHAVIOUR OF HUMIC SUBSTANCES

3.1 General remarks

Humic substances are polyacids which basically contain carboxyl and phenolic OH-groups. In the pH range of natural waters, the carboxyl groups are largely deprotonated (Fig. 19).

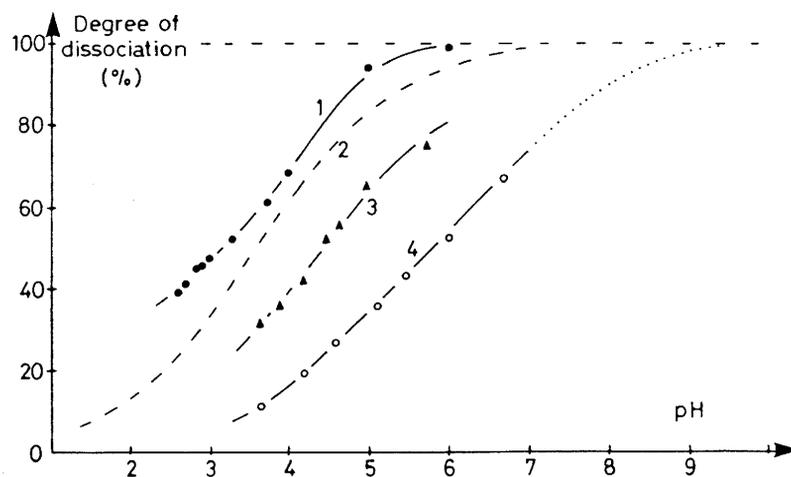


Figure 19: Dissociation of carboxyl groups of natural organic substances as a function of pH. 1: fulvic acid in soil; 2: aquatic organic material; 3: humic acid in peat; 4: macromolecular aquatic material (> 16,000 D) /14/.

The description of the protolytic behaviour of humic substances is complicated by their macromolecular character and non-uniform structure and the models used for this purpose vary correspondingly. If, however, one returns to basic assumptions, then two mutually exclusive boundary concepts can be distinguished:

- a) The polyelectrolyte models proceed on the assumption that all carboxyl and phenolic OH-groups have each the same acidity constant. The effects of substituents are ruled out and the fact that the acidity decreases with progressive neutralisation is attributed solely to electrostatic interactions.
- b) The chemical models view humic acids in the extreme case as a mixture of low molecular weight, simple acids. The acidity of the functional groups is influenced only by adjacent substituents and not by the degree of neutralisation, i.e. not by electrostatic effects.

Since it is not possible on the basis of titration to differentiate conclusively between a polyelectrolyte and a mixture of monoprotic acids /95, 96/, the protolytic behaviour of humic substances can be described satisfactorily by both of these basic concepts. However, a model is not only required to reproduce a titration curve but should also be consistent with chemical intuition.

If a mean molecular weight of 1000 D and a carboxyl content of 5 mmol/g is assumed for fulvic acids, this class of substance can be considered as an acid with five protons and an equivalent mass of 200 D. Such a molecule hardly corresponds to the conventional picture of a polyelectrolyte such as polymethacrylic acid. If one recalls the structural models (section 2.3), then the assumption that the well-separated carboxyl groups have hardly any mutual influence appears to be justified. However, because of the inhomogeneous structure, a large variation in acidity due to substituent influences is to be expected.

If, on the other hand, one considers a high molecular weight humic acid with colloidal dimensions, the picture requires some modification. This can be seen as a three-dimensional gel with a large number of non-identical acid groups which can best be compared with a poorly interlinked ion-exchange resin. The "solution" of such a humic acid is therefore to be seen as two-phase and, in addition to protolysis, Donnan equilibria also come into play. This aspect has been emphasised particularly by MARINSKY et al. /37, 76, 78, 79, 80/.

The theoretical treatment of the polyelectrolytes is discussed in the monograph by KING /61/, while PERDUE /96/ discusses the application of different models to the protolysis of humic and fulvic acids. The models most frequently used are presented briefly here.

3.2 The polyelectrolyte model

This model considers the carboxyl and phenolic OH-groups each to be a uniform class of acids which have the same acidity constant (true or intrinsic constant K_{ai}) on the uncharged molecule. The decrease in acidity of the polyelectrolyte with increasing neutralisation is explained exclusively by electrostatic interactions. This model implicitly assumes that all protolysable groups are in a uniform electrostatic environment. The influence of substituents and intramolecular hydrogen bridges on the acidity are ignored. Although these basic assumptions appear to contradict chemical evidence, the protolytic behaviour of humic substances can frequently be modelled exactly using this approach.

For polyelectrolytes, the apparent acidity constant K'_a depends on the degree of neutralisation α /61/:

$$pK'_a = pH - \log[\alpha/(1 - \alpha)] = pK_{ai} - F\psi / (2.3 R \times T) \text{ with } \alpha = [L^-] / \{ [HL] + [L^-] \}.$$

F is the Faraday constant and ψ is the difference in potential between the polyelectrolyte surface and the solution. For many polyelectrolytes, a linear relationship exists between pK'_a and α (i.e. $pK'_a = pK_{ai} + n\alpha$) so that pK_{ai} can easily be determined by extrapolation to $\alpha = 0$. Figure 20 shows the application of this procedure to a humic acid /23/. Chemically reasonable pK_{ai} values result for both the carboxyl groups and for the phenolic OH-groups. For a series of aquatic humic and fulvic acids, linear extrapolation yielded pK_{ai} values between 2.2 to 2.6 for the carboxyl groups /97/. In a later work from the same institute but by different authors /90, 91/, a mixing model was applied to the same substances with equal success.

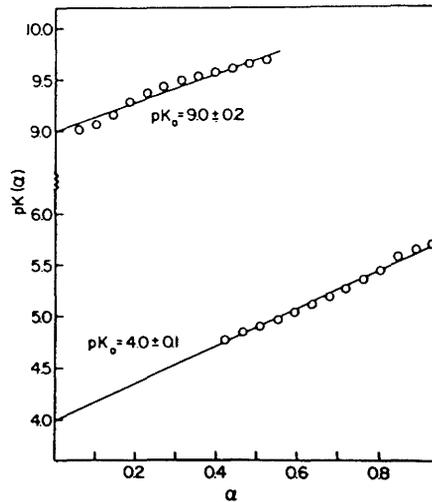


Figure 20: The dependence of apparent acidity constants of the carboxyl and phenolic OH-groups of a humic acid on degree of dissociation α /23/.

The linear relationship between pK'_a and α for humic substances is not universally true. Numerous exceptions can be found in the literature (e.g. /37/) and the determination of pK_{ai} then becomes a problem. Application of the polyelectrolyte model to fulvic acid in one case gave a chemically unreasonable value of $pK_{ai} = -1$ /46/.

The model of MARINSKY et al. /37, 76, 78-80/ is also based on the concept of uniform pK_{ai} values. However, the model also takes a Donnan potential into consideration, which is relevant if the polyelectrolyte is present as a gel phase.

3.3 Mixing models

In this case, humic substances are regarded as a mixture of a few simple protolytes between which electrostatic interactions are ruled out. In most cases, a selection of three to six acids is sufficient for modelling the titration curves successfully.

SPOSITO /107/ simulates the titration curve of a fulvic acid with three pK_a values (4.06, 6.55 and 9.30). PAXEUS and WEDBERG /90, 91/ model the protolytic behaviour of a fulvic acid with five defined acids (salicylic acid, acetic acid, alizarin S, Kojic acid and 1-naphthol). In one of the acids investigated, 5 % of the functional groups were identified as secondary amines. Because this class of substituents is deprotonated in the same pH range as phenols, it was not taken into consideration in the model solution.

EBERLE and FEUERSTEIN /36/ simulate the protolytic behaviour of a humic acid with a discontinuous spectrum of pK_a values which showed six maxima for pK_a at 2.85, 4.30, 5.40, 6.50, 7.5 and 9.0.

These models suggest that only a few defined classes of acid groups are present, but this contradicts the structural variety of humic substances. For this reason, the models are chemically insignificant /96/.

A mixing model based on defined compounds should also be capable of describing the complexation behaviour of polyacids, but it is unlikely that this goal will be achieved.

3.4 The Gaussian distribution model

Several continuous distribution models have been suggested in the literature /96/. The model outlined by PERDUE /93, 95, 96/ has the advantage of being relatively simple but, nevertheless, chemically reasonable. It assumes that the protolytic behaviour of humic substances is determined solely by carboxyl groups and acid OH-groups.

A compilation of pK_a values for acids containing only C, H and O shows a distribution spectrum for carboxyl and phenolic OH-groups, each with one maximum value (Fig. 21). This distribution of the acidity constants reflects the diversity of structural and electrostatic influences. It is assumed that these influences are equally diverse on the protolysis of the acid groups of the humic substances and, as an approximation, a Gaussian distribution of the pK_a values is introduced for the carboxyl and phenolic groups.

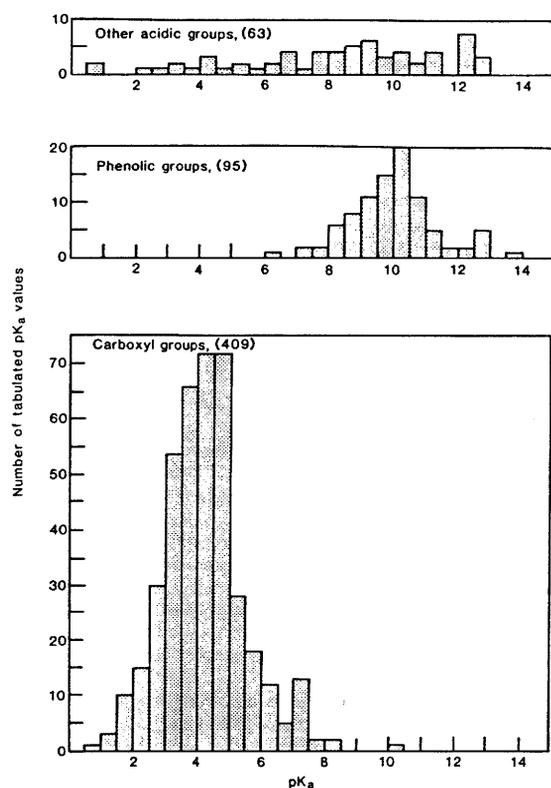


Figure 21: The distribution spectrum of tabulated pK_a values of simple organic acids containing only C, H and O /95/

The modelling of a titration curve requires 2x3 adjustable parameters, i.e. for both protolyte classes the number of functional groups in the fulvic acid, the mean pK_a value and the standard deviation for the distribution of these values.

Figures 22 and 23 show the good agreement between model calculation and titration curve, as well as the distribution of the pK_a values. The model calculation gives a carboxyl content of 5.3 mmol/g and a phenolic OH content of 5.1 mmol/g, which agrees with independently measured values (total acidity: 10.4 mmol/g; -COOH: 4.4 - 6.3 mmol/g; $\text{O}-\text{OH}$: 6.0 - 4.1 mmol/g). In Figure 22, the high mean value of 12.5 for the OH-groups is noticeable. The authors assume that less acidic carbohydrate OH-groups have also been titrated.

The strength of this model lies in the fact that not only does the bimodal Gaussian distribution of the pK_a values reproduce the experimental data exactly but all the parameters in the model also have a real chemical significance. Furthermore, the incorporation of this model into chemical speciation codes such as MINEQL does not present any difficulties /95/.

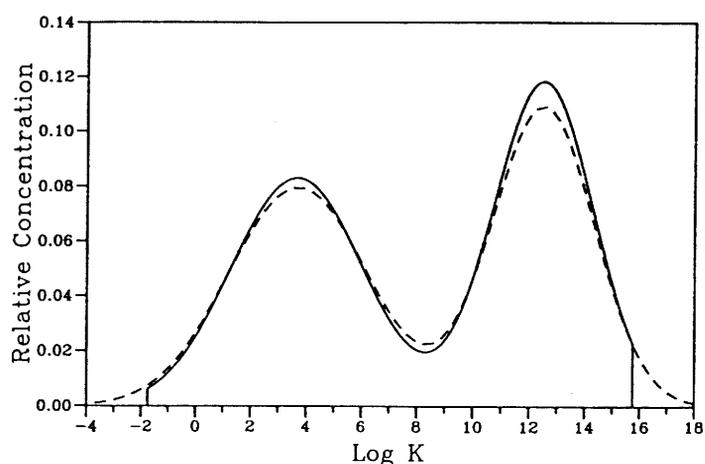


Figure 22: Calculated frequency distributions for acidic functional groups of an aquatic humic acid (truncated and non-truncated bimodal Gaussian distribution) /95/.

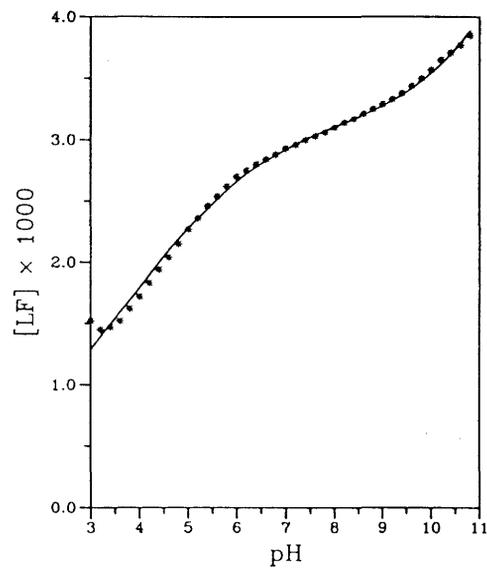


Figure 23:

Experimental titration curve for an aquatic humic acid (dots) and its modelling with the bimodal normal distribution model. [LF]: concentration of deprotonated ligand /95/.

4. HUMIC SUBSTANCES AS LIGANDS

4.1 Introduction

As was shown in the previous chapter, the protolytic behaviour of humic substances is determined mainly by only two functional groups. However, because of the variety of potential substituent influences, it is not possible to give an elementary description of the acid-base behaviour of this class of substance. Simplified models therefore have to be used, which gives rise to the unsatisfactory situation that different models based effectively on contradictory assumptions can give a sufficiently accurate analysis of the experimental results.

Because complexation is influenced not only by the functional donor groups but also by their steric arrangement, it is to be expected in this instance that a full description of behaviour will not be possible. Investigations of the nature of metal bonding in humic substance complexes are rare /111, 66/ and, in natural waters, mixed complexes with inorganic ligands will also be present /13, 18, 19, 72/.

Nevertheless, it is possible to make some qualitative statements as to the complexes to be expected. As chelating agents, phthalic acid- and salicylic acid groups (Figure 24) and catechol (1,2-dihydroxy benzene) represent strong ligands. Substituted diphenols form stable complexes with iron(III) and plutonium(IV) /34/. Tiron is used as a colour indicator in the complexometric determination of iron and can be considered as a model ligand (Figure 24).

The complexes of isolated carboxyl groups are generally unstable. On the other hand, hydroxycarbonic acids, ketonic acids and aliphatic dicarbonic acids come into question as ligands.

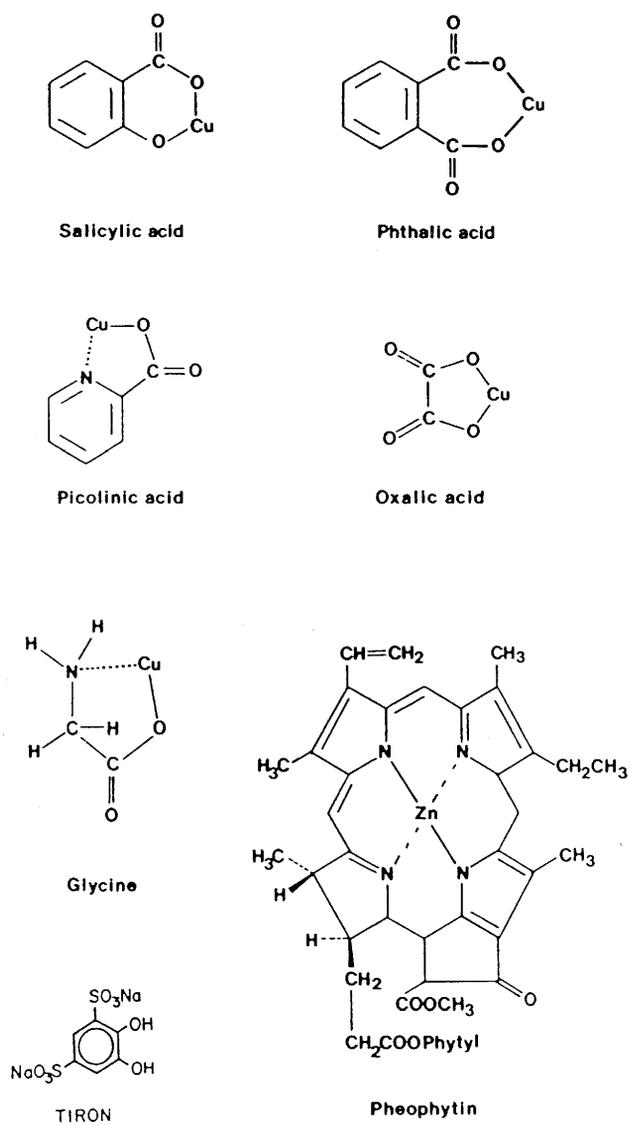


Figure 24: Structures of typical chelating agents. The donor group of the pheophytin is the porphyrin ring /118/

Although the nitrogen content of humic substances is generally low (Tab. 1), this element is a potential donor atom for cations with B-behaviour. Besides aliphatic and aromatic amino groups, amino acid groups or substituted heterocycles such as picolinic acid can be present. It has been demonstrated by means of electron spin resonance that copper is present as a porphyrin complex in terrestrial humic acids. The porphyrin component of humic substances is certainly low and it is not expected that this type of ligand will be measured in titration experiments (see section 4.4). However, since many porphyrin complexes are extremely stable, they can be important for the complexation of metals which are present in extremely low trace concentrations.

Hydroxamic acid groups [-CO-N(OH)-] are presumably responsible for the fact that iron(III) cannot be separated quantitatively from humic substances even at pH 2 /40/. Stable complexes are also formed with plutonium(IV). Since hydroxamic acids are bacterial excretion products /48/, it is to be expected that they will be incorporated into humic substances. In marine fulvic acids, the hydroxamate content reaches around 0.08 mmol/g /68/.

4.2 The definition of formation constants

In experiments designed to investigate complexation by humic substances, the only parameters which are known are the total and the free metal ion concentration (M_t and $[M]$ respectively) and the amount of humic material present (in g DOC/litre; possibly also in moles of humic material per litre if using a mean molecular weight). The concentrations of the individual ligands or sites $[L_i]$ are unknown and the total ligand concentration L_t (in other words the complexation capacity) is at least uncertain. L_t should not be equated with the more easily determinable total acidity. Typically, the acidic groups outweigh the complexing sites by a factor of three or more /35, 119/.

The stoichiometry of the individual complexes is also unknown, but a 1:1 stoichiometry is generally assumed. It is occasionally assumed, however, that complexes with the stoichiometry ML and ML_2 are present (Figure 25). Normally, in the ML_2 complex, both sites are assigned to the same humic molecule. Bridging of two humic molecules via a metal ion is also conceivable, but such bonding is only to be expected in the event of high humic substance concentrations. The bridging leads to flocculation.

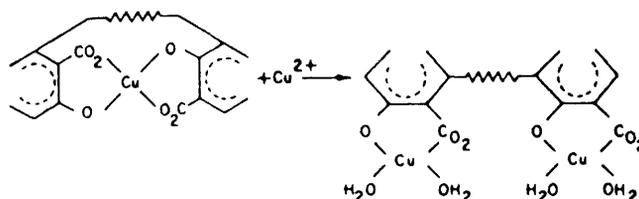


Figure 25: Model concept for the formation of humic complexes with variable stoichiometry (ML and ML_2) /11/

When using complexation constants of humic substances, it should be noted that their formulation is based on only a few measured parameters and many assumptions. Normally, for a series of 1:1 complexes

$$K_i = \frac{[ML_i]}{[M][L_i]}$$

where $[L_i]$ is the free concentration of the i -th ligand.

If 1:1 and 1:2 complexes are assumed, then

$$\beta_1 = \frac{[ML]}{[M][L]}$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2}$$

This interpretation is often chosen for complexation with actinides (section 4.11).

Furthermore, it should be noted that practically all published complexation constants are formal constants and as such are valid only for a specific pH value and a specific ionic strength. It is also worthwhile checking whether additional cations (e.g. Ca, Mg) and ligands (e.g. carbonate) were present in the test solutions.

Occasionally, complexation by humic substances is also described using so-called "mean" constants:

$$\bar{K} = \frac{\sum [ML_i]}{[M] \times \sum [L_i]} = \frac{M_t - [M]}{[M] (L_t - M_t + [M])}$$

(where $\sum [L_i] = L_t - \sum [ML_i]$ and $\sum [ML_i] = M_t - [M]$)

These "mean" constants have the sole advantage that they can be calculated from measured parameters without making any additional assumptions (disregarding the fact that L_t is uncertain). These constants are subject to even stronger restrictions than the formal constants since they are dependent on the total concentrations M_t and L_t . For an illustration of this situation, reference should be made to /33, 93/ (cf. also section 4.5).

4.3 Complexation models

The different models for complexation by humic substances have been summarised and discussed in various works (e.g. /17, 35, 68, 94, 108/). This overview is restricted to the most important model concepts.

4.3.1 Polyelectrolyte models

Such models assume a single type of ligand and describe complexation with one intrinsic complexation constant, taking into account electrostatic interactions /130/. Although such models are able to reproduce experimental data satisfactorily in different cases, they will not be discussed further at this point because the basic assumptions are too far removed from chemical reality.

4.3.2 Mixing models

In much of the literature, humic substances are treated as mixtures of different ligands which only form 1:1 complexes. Other concepts are based on a variable stoichiometry for the complexes. BUFFLE /12/, for example, postulates complexes with the composition ML and ML_2 with a single type of ligand.

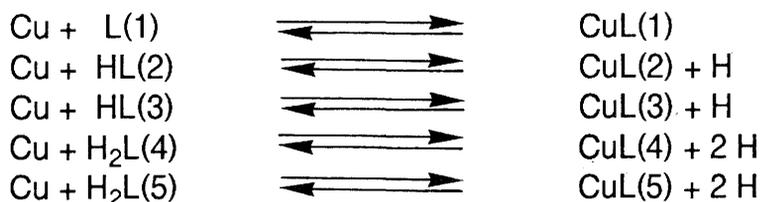
Occasionally, an attempt is made to describe the complexation behaviour of a specific humic substance using a mixture of chemically defined simple ligands. This was successfully applied, for example, in modelling the bonding of copper to a fulvic acid using a mixture of sulphonic acid, dipicolinic acid, 4-aminodipicolinic acid, hemimellitic acid and catechol /46/. This mixture could also be used to describe the protolytic behaviour of the fulvic acid and also reflects its elemental composition.

In general, however, complexation constants and concentrations of single ligands are extracted from experimental data using graphic or numerical methods under the sole assumption of 1:1 stoichiometry (see section 4.5). Usually two, and sometimes three, complexes are sufficient for reproduction of the titration curves. In this case, K_i and the concentrations of the single ligands are adjustable parameters which describe the experiment but are not actually real in chemical terms. Such models do not therefore allow any extrapolation beyond the concentration ranges being investigated /94/.

The somewhat naive view that humic substances contain only two or three different ligands is sometimes weakened by the additional assumption that the individual K_i and L_i values represent **mean values** for ligand **classes**. This does not improve the chemical significance of the model: mean or average formation constants change with the concentration ratios /93, 94/.

These simple mixing models always result from a curve fitting procedure. They are therefore empirical but have the advantage of being easily incorporated into speciation codes. Because such models are often the subject of overinterpretation, they will be discussed in more detail in section 4.4. using a hypothetical example.

The mixing models generally relate to solutions with constant pH value. The model of CABANNIS and SHUMAN also takes into account the influence of pH and ionic strength /21/. Five different ligands were required for modelling the formation of copper-fulvic acid complexes:



This model can be used to interpolate the complexation behaviour of different fulvic acids for pH values of 5 to 8.5 with total copper concentrations of 10^{-7} to 10^{-4} M and fulvic acid contents between 1 and 10 mg DOC/litre.

4.3.3 Affinity spectra

If it is assumed that a large number of discrete ligands with differing concentrations are present, then plotting their frequency against $k = \log K$ results in a spectrum /104/.

The evaluation of the formation function (see section 4.5)

$$\tilde{n} = \int_{-\infty}^{+\infty} N(k) \frac{10^k [M]}{1 + 10^k [M]} dk$$

is via an approximation which includes the differentiation of the formation curve ($d\tilde{n}/dpM$) /35/. The peaks in the resulting spectrum $N(k) = f(k)$ therefore correspond to the inflection points of the formation curve (Figure 26). In the ideal situation, the formation constants and the concentrations of the most important ligands can be identified from affinity spectra.

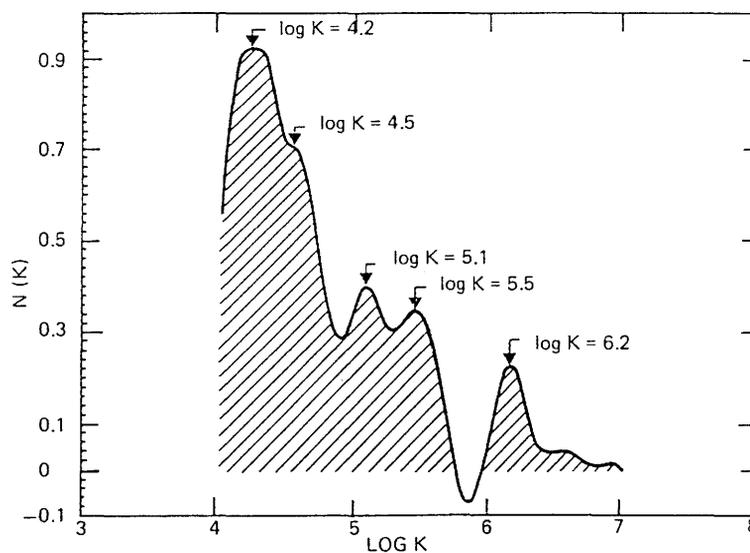


Figure 26: Affinity spectrum for the copper complexes of a humic acid /104/.

4.3.4 The Gaussian distribution model

PERDUE and LYTLE /93, 94/ assume a normal distribution for the mole fraction of ligands:

$$N(k) = [L_i] / L_t = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\mu - k}{\sigma} \right)^2 \right]$$

which is combined with the equation in 4.3.3. σ is the standard deviation and $\mu = \log K_0$.

Evaluation is possible using a curve fitting procedure /35/ or a non-linear optimisation program which adjusts L_t , μ and σ simultaneously /93/.

The complexation of copper by humic substances can be described by means of a simple normal distribution /93/. The assumption of a bimodal distribution improves the description of the experimental data only minimally.

DZOMBAK et al. /35/ have drawn attention to a modified distribution model which requires fewer calculations. It is based on the Sips distribution from which a simple expression for the formation function can be derived analytically:

$$\tilde{n} = \frac{K_o^a [M]^a}{1 + K_o^a [M]^a}$$

where a is a heterogeneity factor ($0 \leq a \leq 1$).

While the assumption of a normal distribution for acid groups can be justified on the basis of Figure 21, such behaviour has not been shown to exist for the ligands. The justification for such an assumption lies purely in the successful modelling of experimental data.

4.4 The titration of ligand mixtures

In order to demonstrate the simple mixing models, it will be shown how a hypothetical polyligand behaves on titration with a metal ion. The parameters selected are typical of a fulvic acid /35/:

$\log K_1 = 10.80$	$\log L_1 = -7.00$
$\log K_2 = 8.80$	$\log L_2 = -6.20$
$\log K_3 = 6.50$	$\log L_3 = -5.20$

The titration curve for the individual ligand is derived from the equilibrium constants

$$K_i = [ML_i] / [M] [L_i]$$

and the rearranged mass balance equations

$$[L_i] = L_{i,t} - [ML_i] \text{ and } [ML_i] = M_t - [M]:$$

$$M_t = \frac{[M] (1 + K_i \times L_{i,t}) + K_i [M]^2}{1 + K_i [M]}$$

$$\text{where } M_t = [M] + \sum_{i=1}^3 [ML_i]$$

the equation for the titration curve of the mixture is

$$M_t = \sum_{i=1}^3 \frac{[M] (1 + K_i \times L_{i,t}) + K_i [M]^2}{1 + K_i [M]} - 2[M]$$

The titration curves for the individual ligands and for the mixture are shown in Figure 27. For $pM_t = -\log M_t$ in the range 4 to 7, all three ligands are required for describing the titration. If it is assumed that the experiments only cover the concentration range $pM_t \leq 6$, then complexes 2 and 3 are sufficient for modelling the titration. It then becomes evident, however, that extrapolation to $pM_t > 6$ gives incorrect values; the complexation is necessarily underestimated. Even with experimental values up to $pM_t = 7$, it cannot be shown that there are no other strong ligands present in small concentrations. As shown in Figure 27, this is only achieved if it can be shown experimentally that pM is proportional to pM_t . This proof fails in practice because of problems with dosing and measuring the free metal concentration.

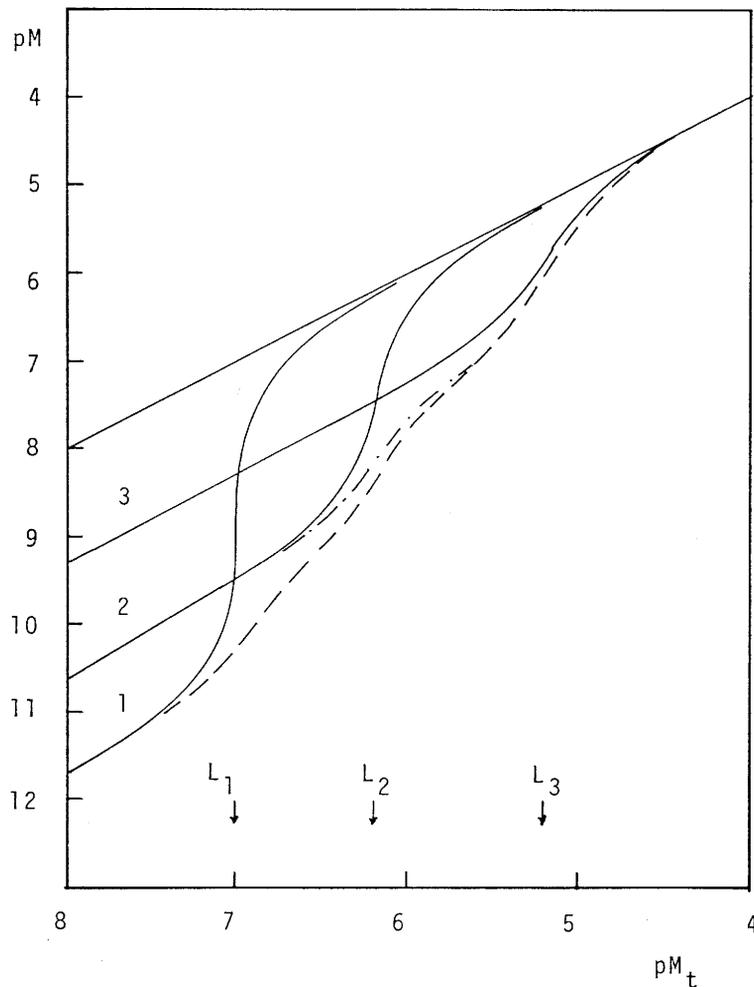


Figure 27: Titration curves for the three individual ligands with concentrations L_1 , L_2 and L_3 .
 --- : summation curve for the ligands 1 to 3;
 -.-.- : profile of the summation curve without ligand 1.

If the same ligand concentration ($L_i = L_t/3$) is assigned to all three complexes, this results in the titration curves shown in Figure 28. The summation curve is now determined predominantly by complexes 1 and 2 and is influenced only slightly by complex 3 in the pM_t range 4.8 to 5.3. Two ligands are therefore sufficient for modelling this system.

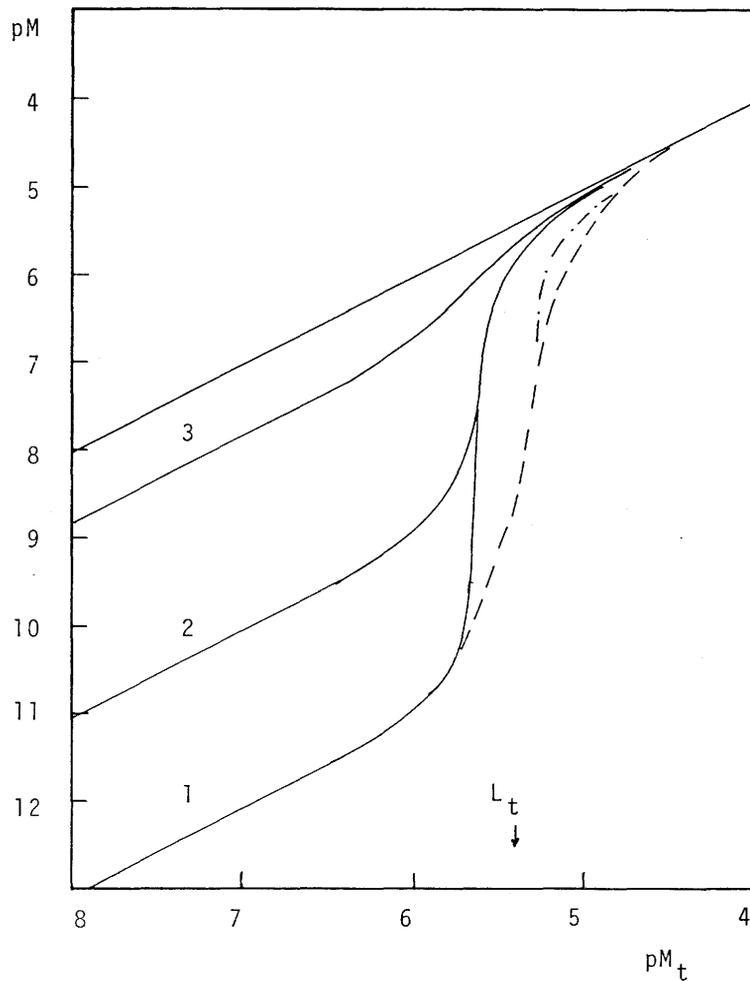


Figure 28: Titration curves for the three individual ligands with concentrations $L_1 = L_2 = L_3$.
 ---- :summation curve;
 -.-.-:profile of the summation curve without ligand 3.

Figures 27 and 28 illustrate the fact that only a proportion of the independent ligands present in a mixture can be identified by the titration experiments. If the amount of metal added is increased, bonding of the ligands occurs in the sequence of their product $K_i \times L_i$. If M_t is smaller than all values for L_i , then the complex with the highest affinity $K_1 \times L_1$ is formed. However, this ligand is "overlooked" in the titration experiment if L_1 is smaller than the lowest metal concentration used in the experiment. On the other hand, weak ligands can be masked even when they are present in relatively high concentrations.

The number of identifiable complexes is therefore limited by the width of the analytical window and by the accuracy of the analytical data. In general, an individual ligand can only be identified if its contribution to the total metal concentration is at least a few percent /35/.

General experience indicates that complexation by humic substances can be described with two to three 1:1 complexes. It follows from the foregoing discussion that this does not exclude the presence of other complexes but rather that the assumption of additional complexes does not significantly improve the data simulation.

The experimental pM_t range generally comprises two to three units. As can be seen from Figure 27, additional ligands are necessary for data simulation if this range is extended. DZOMBAK et al. /35/ estimate that one additional complex is necessary for every order-of-magnitude increase in $[ML] = M_t - [M]$.

For didactic reasons, the example chosen here was clear and simple. A more detailed discussion of the titration of ligand mixtures can be found in GAMBLE and LANGFORD /43/ and PERDUE and LYTLE /94/.

4.5 Evaluation of titration curves

If a titration curve is to be simulated using a number of discrete ligands, the best approach is to use a non-linear optimisation program such as FITEQL /129/. Graphic data evaluation is also possible in principle. In the literature on humic substances, a method originally proposed by SCATCHARD for ion-bonding by proteins is used /102/. Since much of the complexation data for humic substances, particularly the less recent data, was determined using this method, an example is given here.

Complexation constants for 1:1 complexes and the mass balance

$$L_i = [ML_i] + [L_i]$$

are used to define a complexation function \tilde{n}

$$\tilde{n} = \frac{\sum [ML_i]}{L_t} = \sum_i x_i \times \frac{K_i [M]}{1 + K_i [M]} = \frac{M_t - [M]}{L_t}$$

$$\text{where } L_t = \sum_i L_i \text{ and } x_i = \frac{L_i}{L_t}$$

x_i is the mole fraction of the ligand i .

Division by $[M]$ yields the SCATCHARD function

$$\tilde{N} = \frac{\tilde{n}}{[M]} = \sum_i \frac{x_i K_i}{1 + K_i [M]}$$

For the single complex, \tilde{N} is a linear function of \tilde{n} :

$$\tilde{N}_i = x_i K_i - \tilde{n} K_i$$

Figure 29 shows the SCATCHARD diagram calculated using complexes 2 and 3 from the model example discussed earlier. This shows that the summation curve is made up of the SCATCHARD lines for the two single complexes. Reference should be made to /17, 62/ for a more detailed mathematical discussion of the summation curve. In practice, it is difficult to determine the axis intercepts exactly (Figures 30 and 31). The graphic analysis of SCATCHARD diagrams has therefore been repeatedly criticised (e.g. /35/ and particularly /63/) and their application must now be considered bad practice.

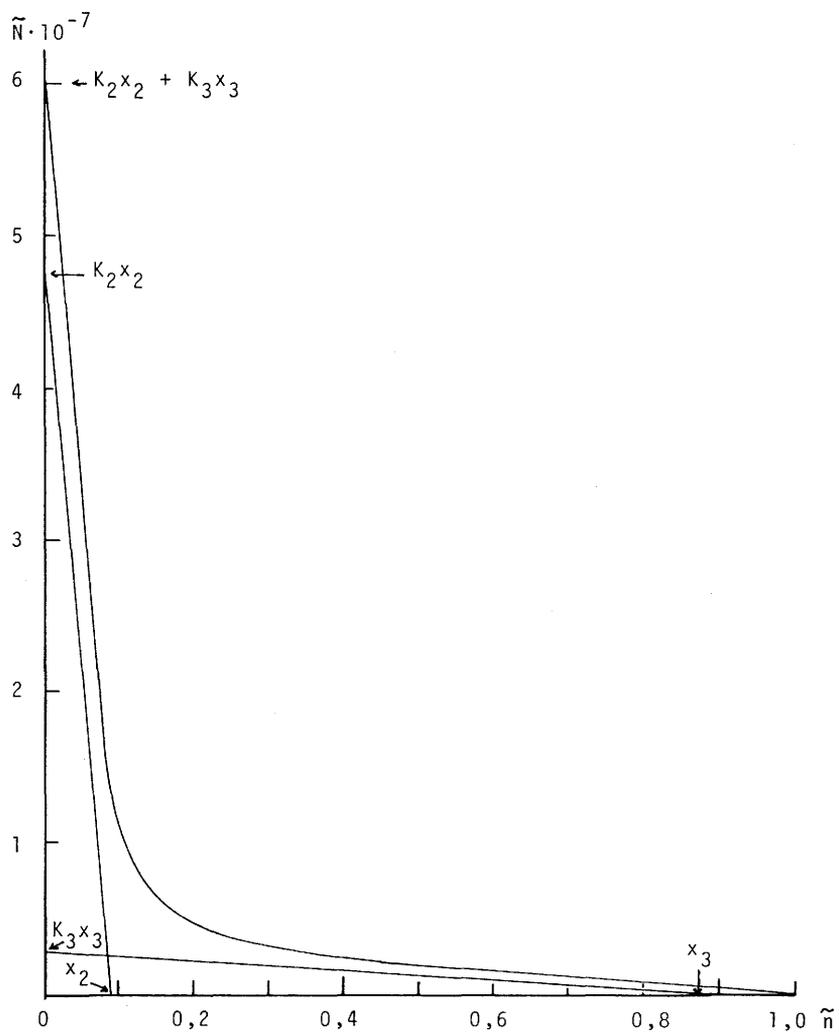


Figure 29: The SCATCHARD functions for the individual ligands 2 and 3 (straight lines) and for the ligand mixture (curve).
 $\log L_2 = -6.20$; $\log L_3 = -5.20$.

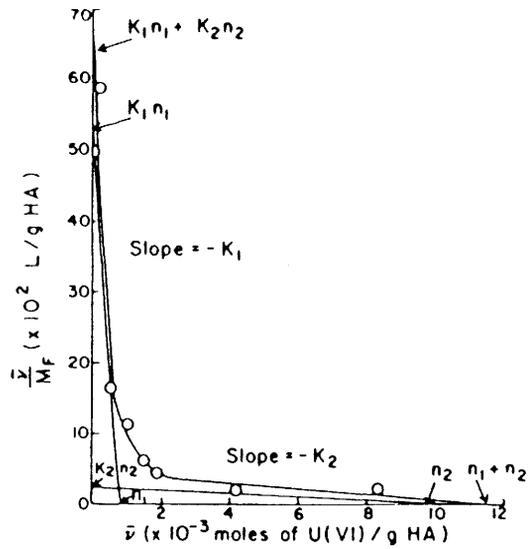


Figure 30:

The interpretation of experimental data for the complexation of uranium(VI) by a humic acid at pH = 6 according to SCATCHARD /70/. The small number of experimental points should be noted.

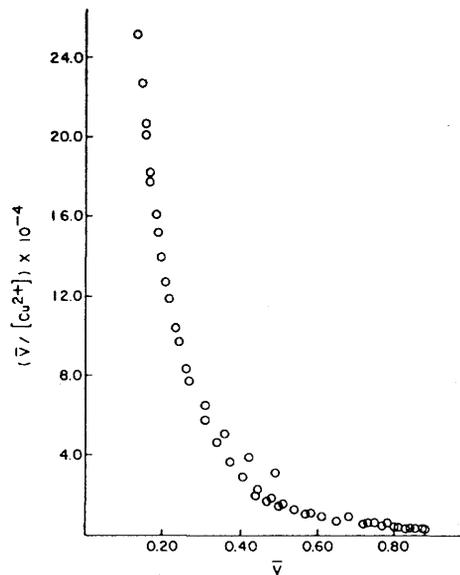


Figure 31: SCATCHARD diagram for the titration of copper with a fulvic acid at pH = 5 (four separate experiments with different copper concentrations /11/).

Determining the total ligand concentration L_t is particularly problematic. It is often impossible to achieve saturation of all ligands in the experiment. In addition, for high values of \bar{n} significant errors can occur because $M_t - [M]$ is the difference between similar numbers. The formation functions $\bar{n} = f(pM)$ are therefore inaccurate (Figure 32). The differences in formation functions are generated solely by using different methods (FITEQL, graphic, experimental) to determine L_t .

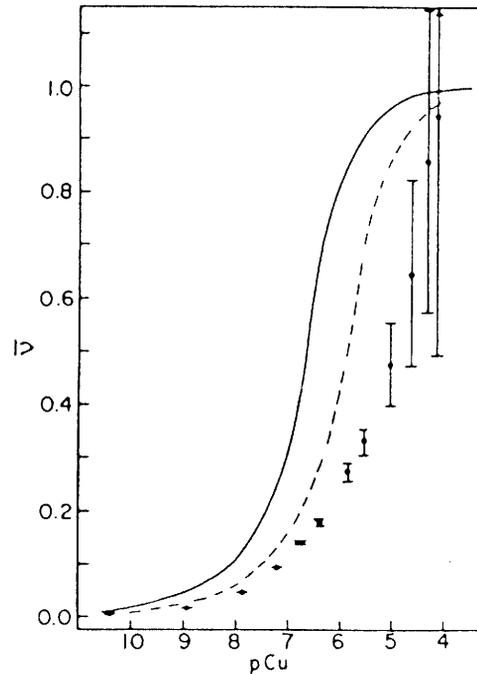


Figure 32: Formation functions \tilde{n} as a function of pCu (fulvic acid with copper at pH = 6). An error band of $\pm \sigma$ is shown for the experimental points. Three 1:1 complexes are taken into account in the calculated curves. Solid line: graphic evaluation. Dotted line: evaluation with FITEQL /35/.

It can also be seen from Figure 29 that the "mean constants" mentioned in section 4.2 are not in fact constant. It follows from the equation for defining \tilde{n} that

$$\sum_i [L_i] = \sum_i [ML_i] (1 - \tilde{n}) / \tilde{n}.$$

If this expression is included in the equation for the mean formation constant (p. 37) and account is also taken of the fact that $\bar{n}/[M] = \tilde{N}$, it finally follows that

$$\bar{K} = \frac{\tilde{N}}{1 - \tilde{n}}$$

The value of \bar{K} therefore changes continually during the titration.

4.6 Comparison of different models

DZOMBAK and co-authors /35/ have compared the most important complexation models with one another using different data-sets (Table 6). The synthetic data-set 1 includes six ligands, ligands 2, 3 and 4 being typical of fulvic acids. In addition to this, a strong ligand with a low concentration (1) and two weak ligands with high concentrations (5 and 6) were also selected. Ligands 1, 5 and 6 are not identified in titrations within normal concentration ranges; they were introduced to test the sensitivity of the models to such ligands.

Data-set 2 uses the same ligands as the synthetic data-set 1. However, a limited analytical accuracy such as might be expected in real experiments was assumed. An accuracy of three significant figures was given for M_t , and two significant digits for pM in the mantissa. Experimental data for a fulvic acid titration with copper were used.

Table 6: Data-sets used for the model comparison by DZOMBAK et al. /35/. L: ligand concentration

	Data-set 1	Data-set 3	Data-set 4
log K ₁	15.0		
log L ₁	-10.0		
log K ₂	10.8	10.72	10.83
log L ₂	-7.0	-6.84	-6.95
log K ₃	8.8	8.29	8.80
log L ₃	-6.2	-5.87	-6.17
log K ₄	6.5	5.94	6.48
log L ₄	-5.2	-5.04	-5.17
log K ₅	4.0		
log L ₅	-5.0		
log K ₆	3.0		
log L ₆	-5.3		
L _t (μM)	22.1	10.6	7.55

The experimental data were evaluated using the SCATCHARD method and assuming three different ligands (Data-set 4). The titration curve could be reproduced accurately using this approach (Figure 33). Graphic analysis results in a total ligand concentration which is considerably smaller than the value which results from an estimation of the complexation capacity (ca. 20 μM).

The numerical analysis of the experimental data with the FITEQL code - again under the assumption that three ligands are present - yields similar results to those obtained with the graphic method (Data-set 3).

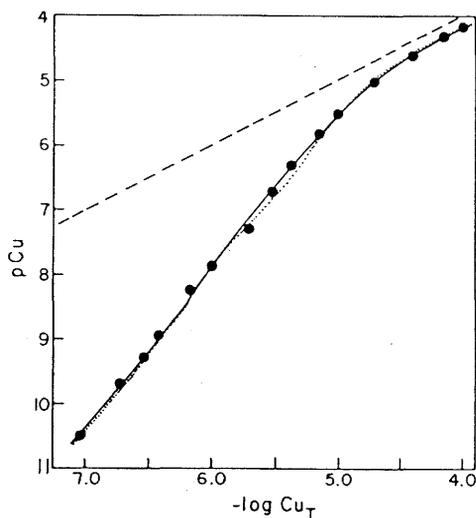


Figure 33: Experimental titration curve for a fulvic acid (5.0 mg C/litre) with copper at pH = 6.0 (points) and modelling with data-sets 1 (-----) and 3 (—) /35/.

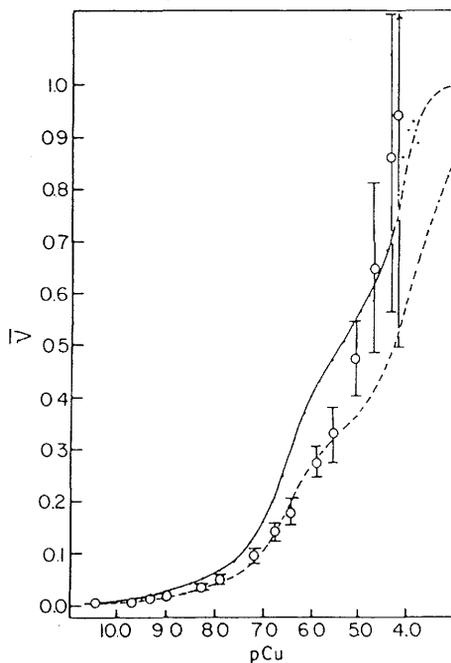


Figure 34: The formation function \tilde{n} as a function of pCu for data-set 1 (-----) and for the "error-ridden" data-set 2 (—). The experimental values are shown with an error band of $\pm\sigma$ /35/.

Data-sets 3 and 4 give very similar titration curves but there are significant differences in the complexation function \bar{n} (Figure 32) which originate from the different total ligand concentrations. If one also compares the formation functions calculated with data-sets 1 and 2 (Figure 34), then the influence of L_t becomes even clearer. When comparing different works it is therefore better to rely on titration curves rather than on formation functions.

The synthetic data-set 1 gives an affinity spectrum with three peaks corresponding to the ligands 3, 4 and 5 (Figure 35 A). Because a limited experimental range of 3.5 to 10.4 was assumed for pM when calculating the spectrum, the ligands 1, 2 and 6 do not show up. For data-set 2, i.e. with assumed inaccuracies for M and pM , a complicated spectrum results (Fig. 35 B), which does not show any particular similarity to spectrum A. The rounding errors alone result in small changes in the gradient of the formation curve, leading to a large number of false peaks in the affinity spectrum. LEUENBERGER and SCHINDLER /69/ have also illustrated this situation. Application of the model to the experimental data is therefore particularly problematic (Fig. 35 C).

Under ideal conditions, individual ligand classes can be identified with an affinity spectrum. However, when applied to experimental data, the spectrum is so strongly fragmented by random errors that it no longer reflects chemical reality.

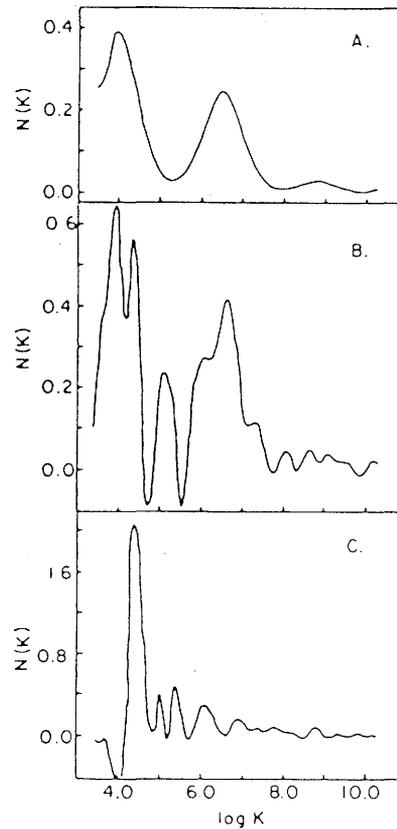


Figure 35: Affinity spectra for data-set 1 (A), for the "errorridden" data-set 2 (B) and for the experimental data (C) /35/.

Modelling of the different data-sets with a normal distribution model was undertaken with curve fitting and a non-linear optimisation program which adjusts L_t , μ and σ at the same time. All of the data could be modelled satisfactorily using the values from Table 7.

However, the normal distribution model produces phantom ligands with $\log K < \mu$, whose existence cannot be verified with titration experiments. By way of an illustration, the normal distribution of $\log K$ was segmented into a hypothetical system of 17 ligands (Fig. 36). The metal speciation for different M_t values was calculated with the MINEQL program and the concentration of the individual complexes was plotted as a function of the formation constants. This shows that ligands with $\log K < \mu$ make no notable contribution to the total concentration. The results in Figure 36 B can be reproduced exactly with nine ligands with $\log K \geq \mu$.

Table 7: Optimum parameters for the unimodal Gaussian distribution with different data-sets /35/.

Data-set	Curve-fitting		Non-linear optimisation	
	μ	σ	μ	σ
1	4.25	1.2	4.45	1.96
2	5.35	1.5	5.42	1.49
2*	-	-	4.41	1.99
3	5.00	1.6	5.13	1.29

*) $L_t = 22.1 \mu\text{M}$

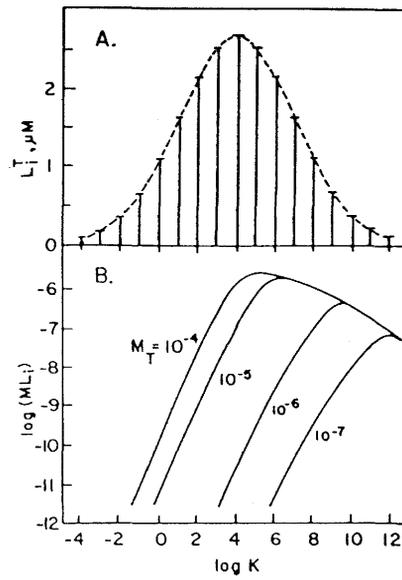


Figure 36: A: 17 discrete ligands with a normal distribution of $\log K$.
 B: The influence of the individual ligands on metal speciation for different values of M_T . $L_t = 2 \times 10^{-5} \text{ M}$ /35/.

TURNER et al. /125/ carried out a similar model comparison. Of the five models tested (electrostatic model; mixing model; variable stoichiometry model; affinity spectrum; normal distribution model), a simple mixing model with two ligands proved to be the best. The models were applied to two experimental data-sets (complexation of copper and lead).

As was the case in reference /35/, it is also confirmed in this work that affinity spectra can be so strongly distorted by random errors that chemically meaningful statements are no longer possible. The assumption of a variable stoichiometry (1:1 and 1:2 complexes) resulted in relatively poor modelling of the experimental data.

CABANNIS et al. /20/ used different models to simulate the complexation of copper by a humic fraction. The experimental data are best reproduced with a mixture of three 1:1 complexes (Tabs. 8 and 9). If the first two primitive models are disregarded, the assumption of a variable stoichiometry gives the worst result. It should be noted that a satisfactory fit is also possible with the electrostatic model, although this is based on fundamental assumptions which contradict the other models.

Table 8: Application of different models to the titration of a humic substance fraction with copper /20/. x_i : mole fraction of the sites.

Model	Parameter
1-site	$\log K = 5.01$
2-sites graphic	$\log K_1 = 7.86;$ $\log K_2 = 4.91$ $X_1 = 0.303;$ $X_2 = 0.697$
2-sites	$\log K_1 = 6.44;$ $\log K_2 = 4.74$ $X_1 = 0.194;$ $X_2 = 0.806$
3-sites	$\log K_1 = 8.25;$ $\log K_2 = 6.32$ $X_1 = 0.013;$ $X_2 = 0.192$ $\log K_3 = 4.73$ $X_3 = 0.795$
Gaussian distribution	$\log K_0 = 4.95;$ $\sigma = 0.94$
Affinity spectrum	Peaks at $\log K = 7.7; 7.3; 6.6;$ $6.1; 4.9; 4.2.$
Variable stoichiometry	$\log \beta_1 = 4.17;$ $\log \beta_2 = 3.71$
Electrostatic	$\log K_{i1} = 6.03;$ $\log K_{i2} = 4.62$ $X_1 = 0.483;$ $X_2 = 0.517$

Table 9: Error analysis for the model comparison (Tab. 8). QAW is the quadratic deviation: $QAW = (\bar{n} - \bar{n}_{calc.})^2 / 20$.

Model	QAW	QAW ($\bar{n} < 0.1$)
1 site	9.19 E-2	1.62 E-2
2 sites graphic	5.40 E-2	4.86 E-3
2 sites	1.02 E-3	3.24 E-4
3 sites	7.56 E-4	4.41 E-5
Gaussian distribution	1.64 E-2	1.99 E-4
Affinity spectrum	1.22 E-2	1.08 E-4
Variable stoichiometry	2.03 E-2	1.44 E-3
Electrostatic	1.65 E-2	5.49 E-4

PERDUE and LYTLE /93, 94/ compare their normal distribution model with a 2-site model. It is shown in particular that no extrapolation is possible with the mixing model. Extrapolations with a normal distribution model remain questionable as long as it cannot be demonstrated that the humic substances conform to a Gaussian distribution.

A summary of the work discussed here shows that it is possible to obtain a satisfactory fit between different models and the experimental data. However, these models tend to reflect the fact that the complexation curves can be described by four to six adjustable parameters rather than to reflect chemical reality. If the principle of Occam's razor is applied, simple mixing models probably represent the optimum solution. They also have the advantage that they can be incorporated into speciation programs such as MINEQL.

It should be emphasised once more that the models can only be used for interpolation within the concentration ranges investigated in the experiments. The normal distribution model suggests the possibility of extrapolation, but this is in the nature of a stop-gap.

This section is brought to a close with a quotation from KLOTZ /63/:

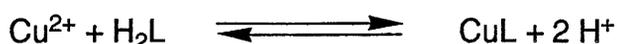
"We would all do well to recall a perceptive admonition made by T.H. Huxley over a century ago: 'Mathematics may be compared to a mill of exquisite workmanship, which grinds you stuff of any degree of fineness; but, nevertheless, what you get out depends on what you put in; and the grandest mill in the world will not extract wheat-flour from peascods, so pages of formulae (or graphs) will not get a definite result out of loose data'."

4.7 The pH-dependence of stability constants

With the exception of MARINSKY's complex model /38/ and the electrostatic model of WILSON and KINNEY /130/, there seem to be no general approaches to providing a quantitative description of the pH-dependence of complexation by humic substances. This is understandable since not only protolysis but also complexation are described using adjustable parameters rather than chemically real acids and ligands.

The pH-dependence of complexation therefore has to be determined empirically, the result again being dependent on the underlying model concepts. An empirical model describing the pH-dependence of complexation over a limited range has been proposed by CABANNIS and SHUMAN /21/(cf. p. 38).

Much of the empirical data applies to the pH range below 5 and is of no interest for this work. Some examples will be selected in the following. DAVIS /31/ determined the apparent stability constants for copper with humic substances from lacustrine sediments in the pH range 4.5 to 9 (Fig. 37). The experimental data were interpreted with a single 1:1 complex. In the pH range 6 to 9, $\text{dlog } K/\text{dpH} = 2.1$, which could be interpreted with the reaction



The release of two hydrogen ions per copper ion is surprising since at pH 7 the carboxyl groups are largely deprotonated (Fig. 19).

Figure 37 also shows the data of BRESNAHAN et al. /11/ for an aquatic and a terrestrial fulvic acid, together with the results from SUNDA and HANSON /115/ for two different organic fractions from rivers. The pH-dependence of these numerical values agrees in qualitative terms with the finding of CABANNIS and SHUMAN /21/ that $\log K/\text{pH}$ is not integral. The data show further that humic substances of different origin behave similarly towards copper.

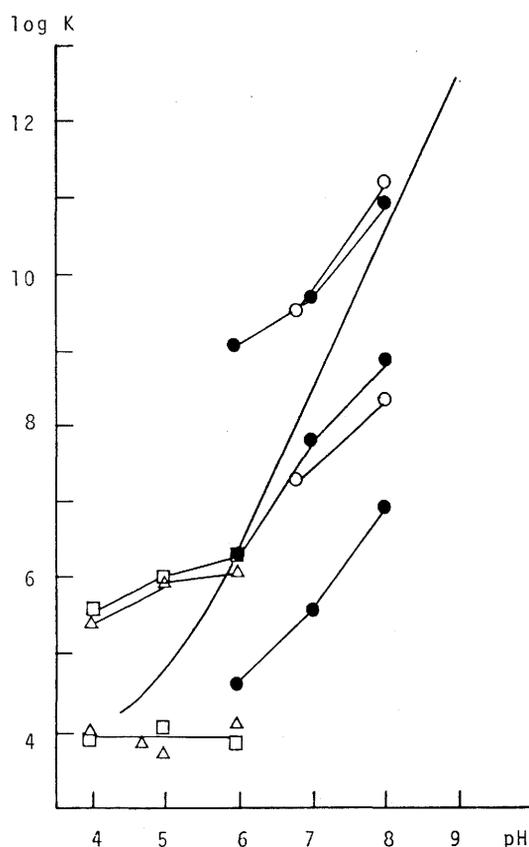


Figure 37: The pH-dependence of the formation constants for copper-humic substance complexes. Line without symbols: /31/ (only one complex).
 ○ , ● : two aquatic fulvic acids (two and three complexes respectively) /115/.
 △ : aquatic fulvic acid (two complexes) /11/.
 □ : soil fulvic acid (two complexes) /11/.

SAAR and WEBER /101/ found that pH had a considerably smaller influence in the case of complexation of cadmium by fulvic acids. In the pH range 4 to 8, $\log K_1$ rises from 3.2 to 4.6 for a fulvic acid from soil and from 3.2 to 4.1 for an aquatic fulvic acid.

Further studies of the dependence of complexation on pH will not be discussed at this point since they contribute very little to an improved understanding of the chemistry of complexation. Figure 38 shows a rather discouraging compilation of complexation data for copper with aquatic fulvic acids. The large scatter is generated by the use of different evaluation methods rather than by differences in the ligand behaviour of humic substances. As BUFFLE has shown, the picture improves if the data are interpreted from a consistent viewpoint /16, 17/.

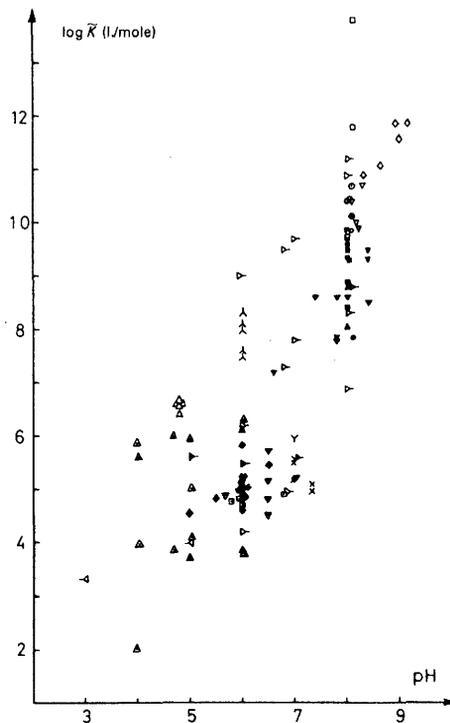


Figure 38: Compilation of complexation constants for copper with aquatic fulvic acids /15, 17/.

Finally, mention should be made of studies which describe the stability constants as a function of the degree of dissociation α of carboxyl groups. They will be referred to later (section 4.11) in connection with the actinides. Considering Figures 37 and 38, it remains questionable whether extrapolation of the formation constants to $\alpha = 1$ (i.e. to pH values of around 7) yields usable values. In some cases, it has been shown that a plateau exists in the log K/pH curve in the pH range between 7 and 9, for example for the fulvic acid complexes of europium(III) /77/ and for the adsorption of americium on a colloidal humic acid /32/.

4.8 The influence of ionic strength

The influence of ionic strength on the protolytic and complexation behaviour of humic substances cannot be described in simple terms since the application of an extended Debye-Hückel approach to macromolecules is not justified.

In general, formal complexation constants decrease with increasing ionic strength (less recent literature in /56/). The influence of ionic strength on the protolysis of humic substances is discussed by EPHRAIM et al. /37/ in connection with the polyelectrolyte model of MARINSKY.

For the complexation of copper, lead and cadmium by humic acids, STEVENSON /109/ finds an empirical linear relationship between log K and the square root of the ionic strength.

CABANNIS and SHUMAN /21/ have shown that the influence of ionic strength on the formation of copper-fulvate complexes depends on pH and also on the total copper concentration. At pH 7.0 and 5 mg DOC/litre, pCu decreases by 1.2 to 1.5 units if the ionic strength is increased from 0.01 to 0.1. At pH 8.44, the effect is smaller (0.7 to 1.0 units), and smaller still at pH 5.44 (0.1 to 0.5 units). The differences between pH 7 and 5.4 can be understood qualitatively in terms of the lower charge of fulvic acid at lower pH values. However, the difference between pH 7 and 8.4 does not fit into this picture.

Surprisingly, the influence of ionic strength at pH 7 (but not at other pH values) can be described with the Güntelberg equation if a formal charge of -5 is assigned to the fulvic acid (Fig. 39). The authors are however aware of the fact that use of the equation is justified only by its success.

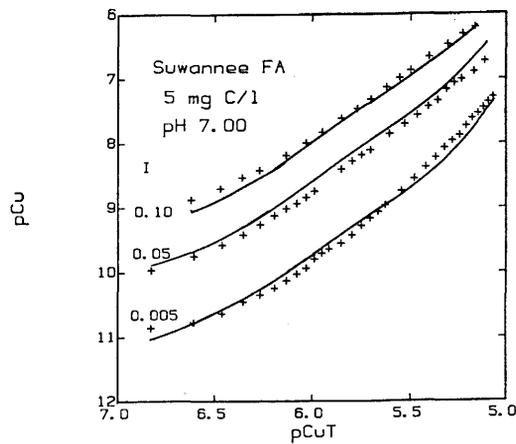


Figure 39: Titration curves for an aquatic fulvic acid with copper at different ionic strengths. The calculated curves take account of the influence of ionic strength with the aid of the Güntelberg equation with $z = 5 / 21$.

4.9 Comparison of different humic substances

To achieve a reliable comparison of metal complexation by humic substances of different origin it is not enough to keep the experimental conditions constant; the same evaluation procedure also has to be used in each case.

McKNIGHT et al. /81/ extracted fulvic acids from 18 different waters and carried out a potentiometric investigation of their complexation with copper at pH 6.25. The metal concentration varied in the range 10^{-7} to 10^{-4} M. The experimental data were evaluated with the computer code FITEQL /129/; a 2-site model proved to be sufficient.

The values for $\log K_1$ varied between 5.4 and 6.6, with a mean value of 6 ($\sigma = 0.29$). The concentrations of the pertinent site L_1 varied from $4.4 \cdot 10^{-7}$ to $1.9 \cdot 10^{-6}$ with a mean value of $(1.0 \pm 0.4) \cdot 10^{-6}$ mol/mg C.

For $\log K_2$ the values lay in the range 7.5 to 8.5 (mean value 8.0; $\sigma = 0.41$). The ligand concentrations range from $1.0 \cdot 10^{-7}$ to $6.5 \cdot 10^{-7}$ mol/mg C (mean value $(2.6 \pm 1.6) \cdot 10^{-7}$).

Under the assumption that the average total acidity (carboxyl groups and phenols) is 8 meq/g, it follows that the L_1 sites represent around 15 %, and the L_2 sites around 5 %, of the functional groups (calculated for bidentate ligands).

The small differences in the complexation behaviour of these fulvic acids show that a model substance can be used as a basis for evaluating their influence on metal speciation. A differentiation according to origin (from soil, water or sediments) seems to be necessary in view of the data in /74/ (Table 10).

CABANNIS and SHUMAN /21/ also determined from the application of their empirical model (p. 39) that samples of humic substances of different origin vary only slightly in their behaviour with respect to copper. They conclude from their results that it would be better to concentrate more on the influences of pH and ionic strength rather than investigating the spatial and temporal variations in the bonding properties of humic substances.

4.10 Comparison of different metal ions

Studies of complexation by humic substances seem to concentrate mainly on copper. Data for lead, zinc and cadmium are somewhat scarcer (cf. the data compilations in /17, 75/). Systematic investigations with a series of different cations and one specific humic substance are extremely rare.

One exception is the work of MANTOURA et al. /74/. Complexation behaviour was investigated at pH 8 using a gel-filtration method /73/. The experiments were analysed graphically with a 2-site model. The log K_0 values given in Table 10 are the arithmetic mean of log K_1 and log K_2 values.

The stability of the complexes generally follows the order



(Irving-Williams series). It should be noticed that only mercury and copper are distinctly different from the other heavy metal ions. Speciation calculations for natural waters show that only these two metals are complexed to any significant extent with humic substances. The other ions are bound to humic substances to an extent of less than one percent.

Table 10: Stability constants (as log K_0) for the complexes of divalent metals with different humic substances (pH = 8, I = 0.02). From /74/.

Humic substance	Ca	Mg	Mn	Co	Ni	Cu	Zn	Cd	Hg
Peat, FA	3.65	3.81	4.17	4.51	4.98	7.85	4.83	4.57	18.3
Peat, HA						8.29			
Lake-water									
L. Celyn 1	3.95	4.00	4.85	4.83	5.14	9.83	5.14	4.57	19.4
L. Celyn 2	3.73	3.67	4.30	4.75	5.27	8.42	5.05	4.70	20.1
L. Bala	3.56	3.26		4.67		9.30	5.25		19.3
River-water						9.48	5.36		19.7
Loch Etive									
Water 1	3.65	3.50		4.29	5.31	8.89		4.95	20.6
Water 2	3.27	3.41		4.75	5.19	10.21		4.87	20.6
Sediments	4.65	4.09		4.91		11.37	5.87		21.3
Sea-water 1	3.60	3.50	4.45	4.83	5.41	8.89	5.27		18.1
Sea-water 2	4.12	3.98	4.51	4.79	5.51	9.71	5.31	4.69	18.0
Mean value									
	3.83	3.70	4.46	4.72	5.26	9.30	5.27	4.73	19.4
Standard deviation									
	0.39	0.28	0.26	0.19	0.18	0.95	0.28	0.16	1.1

4.11 Humic substance complexes of the actinides

The stability constants for humate and fulvate complexes of the actinides have been compiled in a review work /26, 58/ (Tab. 11). These data are widespread throughout the waste disposal literature and are often quoted without the necessary reservations. Above all, it should be noted that, for the calculation of these constants, the total ligand concentration was equated to the concentration of carboxyl groups /26/. There are, however, some uncertainties: in some of the original works, the concentration of ionised groups is given as the reference parameter /24, 85/. Such inconsistencies are surprising, particularly in view of the fact that CHOPPIN is a co-author on three of the publications mentioned. Furthermore, complexes of composition ML and ML₂ are assumed (for definition of the constants cf. p. 37). The data of LI et al. /70/, which assume two 1:1 complexes, have been converted. If one compares the original data (Tab. 12) with the converted values, no similarity can be recognised.

The complexation of the actinides by humic substances has mainly been investigated at low pH values. These data cannot therefore be applied directly to natural waters in the pH range 7 to 8. CHOPPIN et al. /85, 103, 124/ have investigated complexation for different elements as a function of degree of neutralisation α (Fig. 40). The following relationships apply /26/:

$$\begin{aligned} \text{Am(III)}: \log \beta_1 &= 3.5 + 10.9 \alpha; \log \beta_2 = 10.4 + 5.3 \alpha \\ \text{Th(IV)}: \log \beta_1 &= 9.2 + 7.1 \alpha; \log \beta_2 = 14.2 + 7.6 \alpha \\ \text{Pu(IV)}: \log \beta_1 &= 9.8 + 9.0 \alpha; \log \beta_2 = 16.0 + 9.0 \alpha \\ \text{U(VI)}: \log \beta_1 &= 5.0 + 4.8 \alpha; \log \beta_2 = 8.5 + 4.5 \alpha \end{aligned}$$

Extrapolation to $\alpha = 1$ gives constants which are used for speciation calculations in natural waters (e.g. /85/). It is implicitly assumed that the stability constants are no longer pH-dependent if all the carboxyl groups are deprotonated (cf. section 4.7).

Table 11: Stability constants for actinide and europium complexes with humic (HA) and fulvic (FA) acids for ionic strength $I = 0.1$. For data with *, $I = 0.01$. After /58/ (cf. also /26/).

Ion	Ligand	pH	$\log \beta_1$	$\log \beta_2$	
Th ⁴⁺	HS	4.0-5.0	10.74-13.18	15.79-18.43	85
	HS	3.5	-	6.74	53
	FS	4.0-5.0	9.80-10.28	13.45-15.07	85
U ⁴⁺	HS	6.0	6.98*	11.49*	70
	FS	6.0	6.64*	11.58*	70
UO ₂ ²⁺	HS	4.0	5.11	8.94	103
	HS	3.5-7.0	7.8	-	65
	HS	6.0	6.73*	11.44*	70
	HS	5.0	5.68	-	53
	HS	4.5	5.16	9.31	83
	FS	4.5	5.14	9.63	83
	FS	6.0	7.38*	12.94*	70
Am ³⁺	HS	4.5	6.83	10.58	8
	HS	6.5	6.4	10.6	131
	HS	4.7	8.9	12.9	124
	HS	6.0	12.1	14.6	124
	HS	8.0	14.4	15.7	124
Eu ³⁺	HS	4.5	6.08	-	22
	HS	4.5	7.38	10.26	8
	FS	4.5	6.49	10.52	8

Table 12: Stability constants for humic and fulvic acid complexes of uranium(VI) and -(IV) assuming 1:1 stoichiometry C_1 , C_2 : site concentration (mmol/g) /70/.

		$\log K_1$	C_1	$\log K_2$	C_2
UO_2^{2+}	HS	4.72	9.5	6.73	1.0
	FS	5.56	3.8	7.43	0.2
U^{4+}	HS	4.51	4.5	6.98	0.5
	FS	4.94	1.8	6.94	0.3

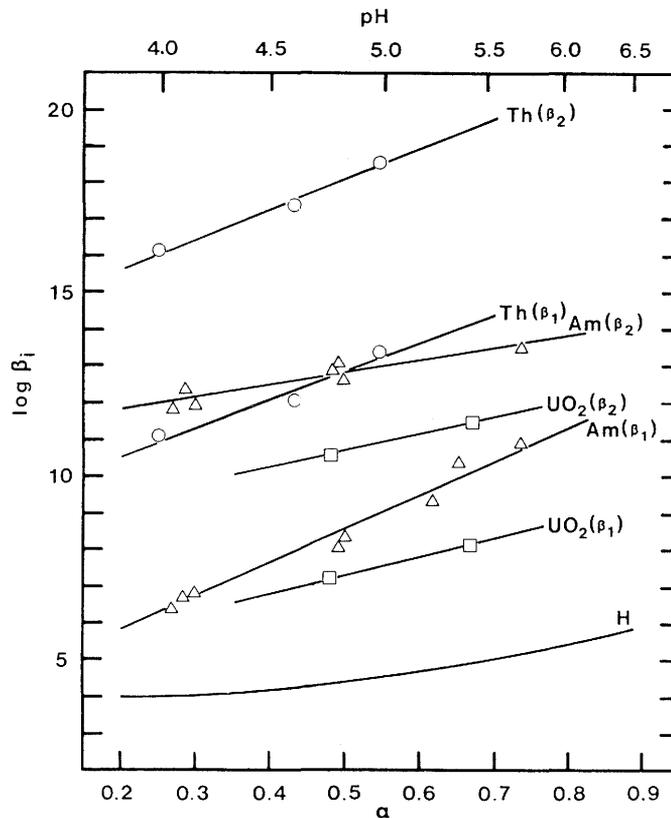


Figure 40: Stability constants for humic acid complexes of some actinides as a function of degree of dissociation α (25°C, ionic strength 0.1) /26/.

It is noticeable in Table 12 that uranium(IV) and -(VI) differ only slightly in their behaviour towards humic substances. This disturbs the chemist who would expect a similarity between uranium(IV) and thorium, and who misses a reference in the work of LI et al. /70/ to the measures taken to exclude oxygen.

GIESY et al. /44/ interpreted their data for uranium(VI) with a three-ligand model. A direct comparison with the constants given in Table 11 is therefore not possible. However, the work is interesting because the influence of humic substances in an acidic DOC-rich water is modelled.

It would be beyond the scope of this work to discuss the influence of humic substances on the geochemical behaviour of the actinides. This topic is dealt with in /47, 98, 132/ with regard to uranium and there are references in /27, 86, 87, 105/ to the transuranics. BOGGS et al. /10/ give a detailed compilation of the literature on the subject.

KIM et al. /59, 60/ have shown for waters from the Gorleben area that the concentrations of tri- and quadrivalent metals show a linear correlation with the content of dissolved organic carbon (DOC) (Fig. 41). There is no correlation for the uranyl ion because the carbonate interferes here as a ligand. As analogue studies, such investigations probably give a better insight into the complexation of fission products and actinides by humic substances than model calculations which use dubious constants.

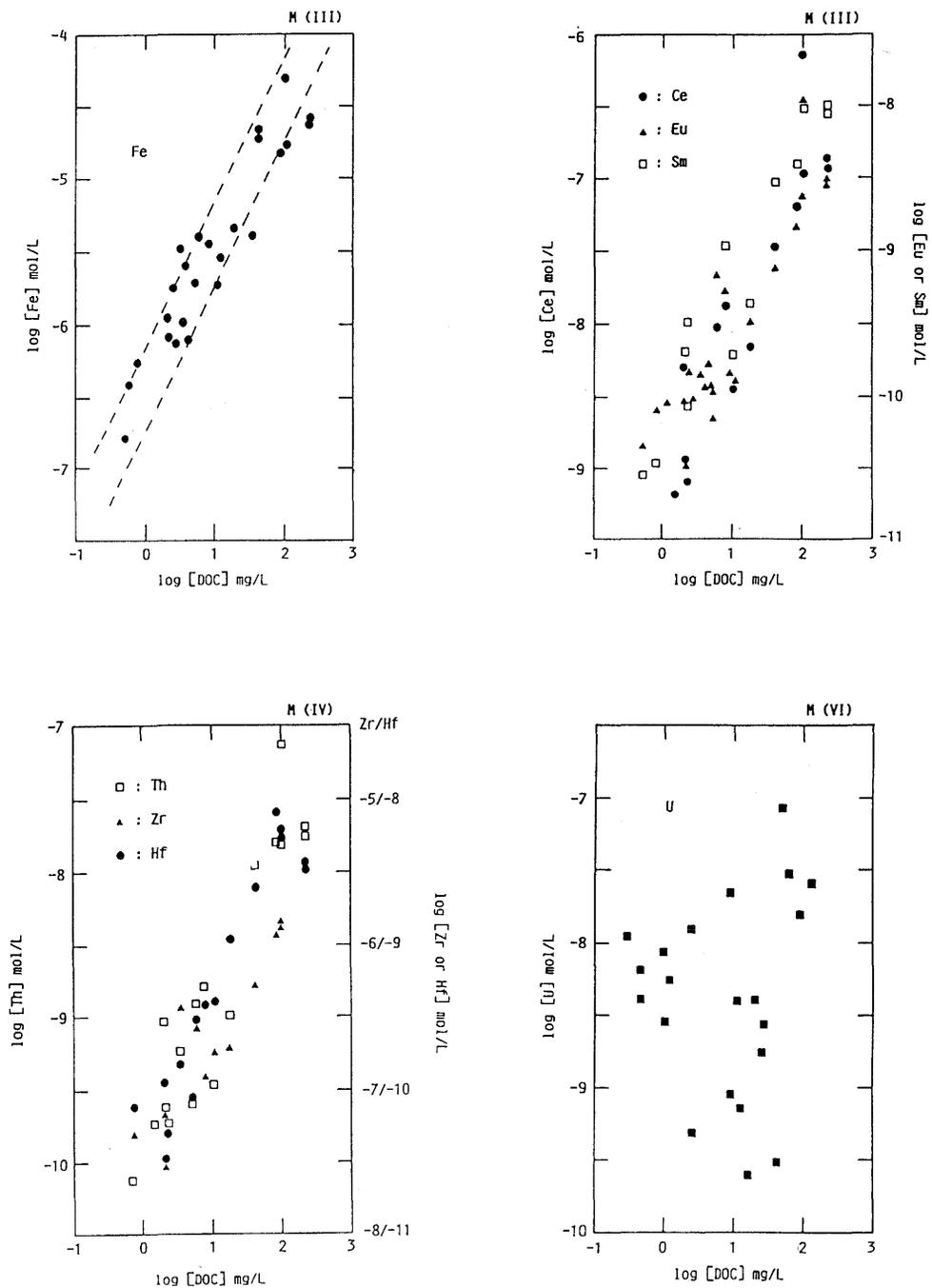


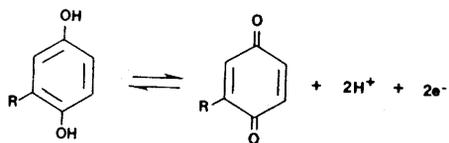
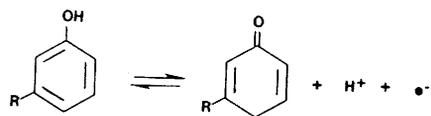
Figure 41: The concentration of iron(III) and trace elements as a function of the content of dissolved organic carbon in different groundwaters from Gorleben /60/.

If, in addition to humic substances, the formation of hydroxo and carbonato complexes in natural waters is taken into account, then - even with all the attendant uncertainties - some qualitative conclusions can be drawn /26/:

- Humic substances can influence the solution chemistry of trivalent actinides even at low concentrations and in the presence of carbonate. By analogy, this should also apply to the trivalent lanthanides (e.g. /124/).
- For the quadrivalent actinides, hydroxo complexes dominate in natural waters and the presence of humic substances in low concentrations is of secondary importance.
- Although the information on pentavalent actinides is only qualitative /86/, competition between humic substances and carbonate as ligands can be assumed.
- For the hexavalent actinides, carbonato or humic complexes can dominate depending on concentrations. For sea-water it is estimated that with 10^{-5} equivalents of humic material per litre, around 50 % of the uranium is organically bound; at 10^{-4} eq/L, the figure is > 98 % /103/. In freshwater, uranium(VI) is present mainly in the form of carbonato complexes /65/ (cf. also /44, 132/). It should however be taken into account that the hexavalent actinides are partly reduced by humic substances (chapter 5).
- The bonding of calcium by humic substances is comparatively weak. CHOPPIN and SHANBAG /25/ therefore come to the conclusion that calcium in the concentration range expected in natural waters does not have a significant effect on the complexation of actinides by humic substances (cf. also /3, 44, 51, 99, 128/).

5. REDOX REACTIONS OF HUMIC SUBSTANCES

As metastable organic compounds, humic substances participate in irreversible redox reactions which, in certain cases (e.g. diagenetic changes), occur very slowly. Phenolic and quinone components can also react reversibly:



For such reactions, a redox potential at pH = 0 of 0.5 V for fulvic acids and 0.7 V for humic acids was estimated /106/. A summary of the literature can be found in THURMAN /118/.

NASH et al. /86/ showed that, in a carbonate/bicarbonate solution, humic acid reduces plutonium(VI) to oxidation state IV and neptunium(VI) to Np(V). Uranium(VI) is not reduced.

Per gram of humic acid, more than 250 meq of plutonium and neptunium were reduced /86/. This high reduction capacity can only be explained by a largely irreversible oxidation of the humic acid.

According to other authors /26/, Pu(VI) is only partly reduced by humic acid in synthetic sea-water to Pu(V).

6. SORPTION OF HUMIC SUBSTANCES ON MINERAL PHASES

The macromolecular humic substances present in waters are adsorbed to a large extent on clay minerals or oxidic solid phases. The chemical properties of the mineral surfaces - particularly their sorption behaviour with respect to metal ions - are modified by the presence of organics.

Humic acids sorbed onto colloids are often considered as humin /117/. Recent spectroscopic investigations have however shown that humin is structurally different from humic acids. Humin should therefore not be considered as a clay-humic acid complex /50/.

Humic substances are sorbed on oxidic materials such as $\gamma\text{-Al}_2\text{O}_3$ /29, 30/ and goethite or hematite /89, 120, 121/ by formation of surface complexes. In 1:1 electrolytes, the amount sorbed decreases strongly as the pH increases (Fig. 42). On the other hand, in the presence of calcium ions, the organic material remains on the oxide surface even at higher pH values (Fig. 43). The sorption of humic acid on goethite is also favoured by the presence of calcium and magnesium ions /120, 121/. This effect of alkaline earth ions explains why hard waters have only a low concentration of dissolved humic substances.

As expected, humic substances are sorbed more strongly as their molecular weight increases (Fig. 44). Such fractionation processes could explain why fulvic acids dominate over humic acids in natural waters.

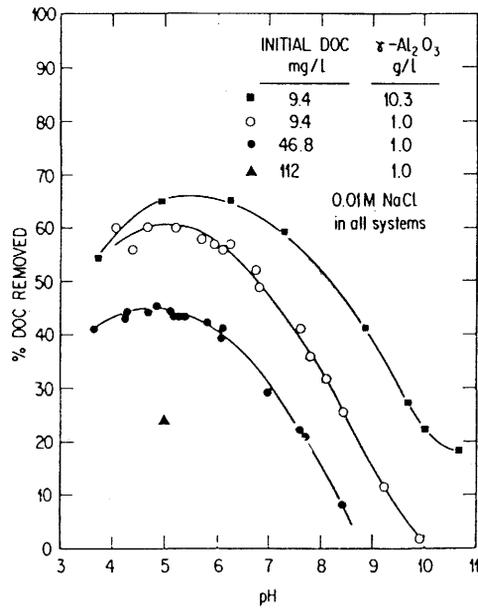


Figure 42: Adsorption of organic sedimentary material (Urnersee) on γ -Al₂O₃ as a function of pH /30/.

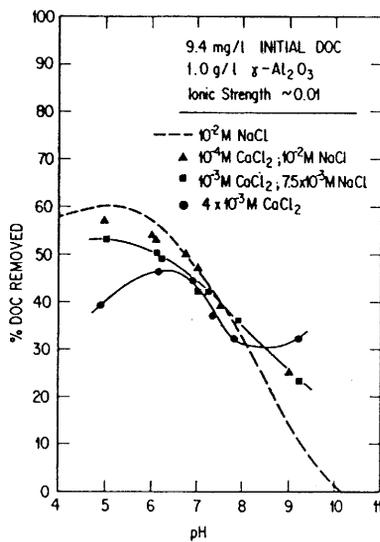


Figure 43: Adsorption of organic sedimentary material (Urnersee) on aluminium oxide in the presence of calcium chloride /30/.

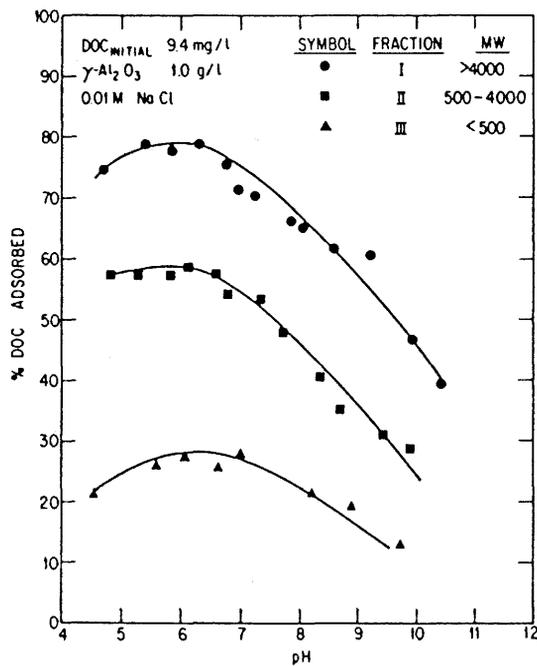


Figure 44: Adsorption of different molecular weight fractions of organic material from Greifensee sediments on γ -Al₂O₃ as a function of pH /29/.

While the sorption of humic acids on oxidic surfaces can be explained qualitatively using established models of formation of surface complexes /112/, other aspects play an important role in the case of sorption on clay minerals. The two-layer silicate kaolinite behaves similarly to an oxide /30/. The three-layer silicates (smectites) have negative layer charges, which makes direct sorption of the negatively charged humic acids more difficult. According to current understanding, sorption of humic acids on these clays is mainly via polyvalent cations and hydrogen bridges (Fig. 45). This would agree with the fact that low molecular weight humic substance fractions with a high specific carboxyl content are sorbed preferentially on clay minerals /98, p. 156/. Sorption is also very dependent on ionic strength (Fig. 46 /98/).

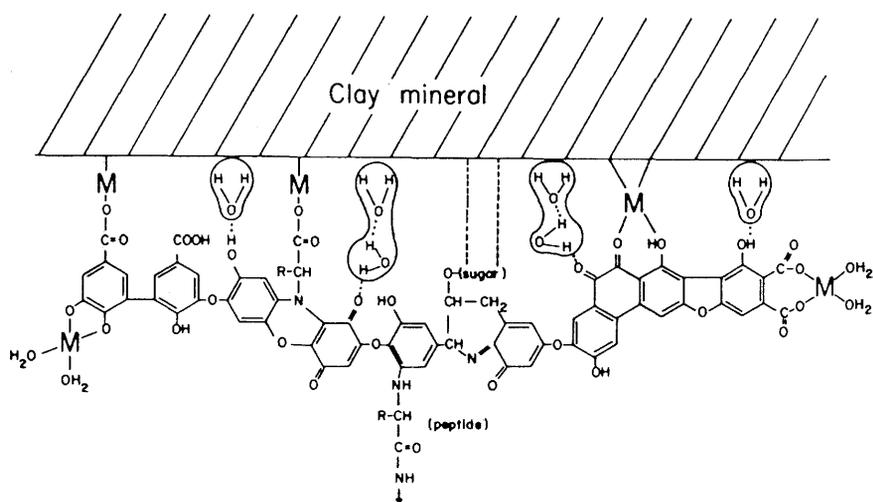


Figure 45: Schematic representation of a clay-humic acid complex in the soil /110/.

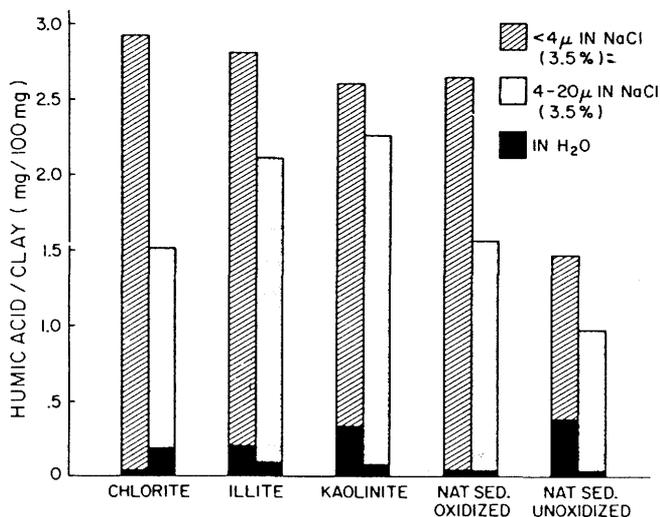


Figure 46: Comparison of the adsorption of a humic acid on two size fractions of different clay minerals and on a natural sediment /98/. The influence of ionic strength should be noted.

The influence of calcium and other cations on the sorption of humic acid on clay minerals has been investigated extensively. The literature is summarised in /117/. By way of example, the systematic investigations by THENG and SCHARPENSEEL /116/ should be mentioned here. These authors saturated montmorillonite with different cations and then investigated sorption of humic acid at pH 7 (Fig. 47). As expected, the trivalent cations are particularly effective. However, under natural conditions, the differences between sodium- and calcium montmorillonite are of particular importance.

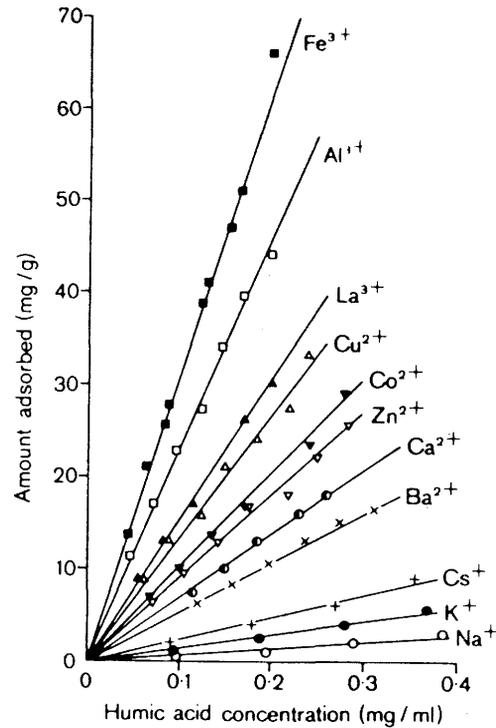


Figure 47: Adsorption isotherms for humic substances on montmorillonite saturated with different cations (pH = 7.0, 25°C) /116/.

Humic substances are also sorbed strongly on calcium carbonate /88, 114/, but sorption on SiO₂ is not so pronounced /30/.

Intercalation, i.e. emplacement of humic acid in the interlayers of the montmorillonite, begins at pH values below 6 and will only lead to significant layer expansion at pH values around 4 /117/.

Sorbed macromolecular humic substances modify the sorption properties of the mineral surfaces and current concepts /112/ are no longer sufficient for describing cation adsorption.

Humic substances are sorbed on oxidic surfaces particularly at low pH values and the organic surface complex can bind cations in a pH range in

which no sorption would occur on the pure oxide. At high pH values, the humic substances are desorbed and become available as dissolved ligands which suppress cation adsorption.

Very few investigations have been carried out in solid/ M^{z+} /humic substance systems. TIPPING et al. /122/ looked at the pH-dependence of copper adsorption on goethite in the presence of humic substances, while HO and MILLER /52/ describe the influence of humic acid on the sorption of uranium(VI) on hematite. Similar work by BIDOLGLIO et al. /9/ deals with plutonium and neptunium.

Figure 48 was taken from the work of DAVIS /31/ and shows the sorption of copper on aluminium oxide with and without humic substances from sediments (the sorption of humic substances on the oxide is shown in Figure 42). In the pH range of natural waters, copper adsorption decreases with increasing humic material content and the metal remains in solution as a humic complex. DAVIS has developed a model which provides a satisfactory description of the experimental data (Fig. 49).

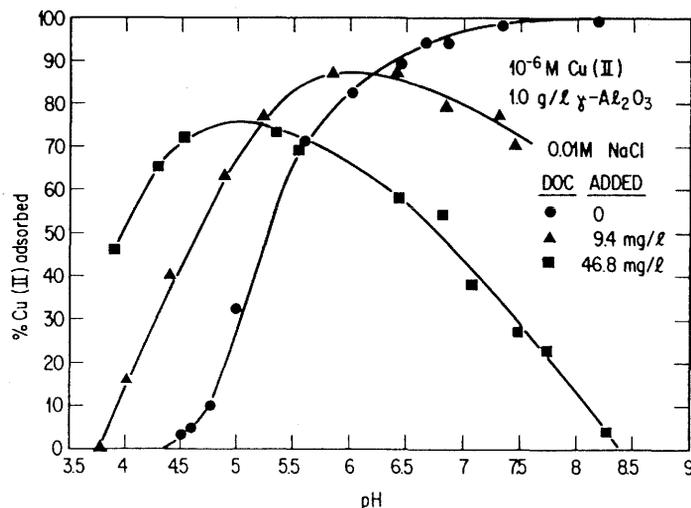


Figure 48: Adsorption of copper on aluminium oxide in a pure NaCl-solution and after addition of humic substances as a function of pH /31/.

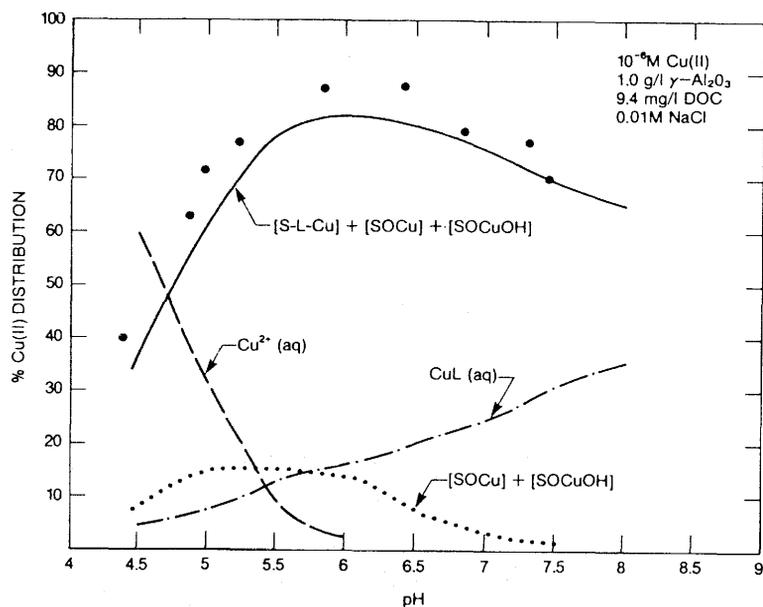


Figure 49: Modelling of the distribution of copper between aluminium oxide and the solution in the presence of humic substances. Points: experimental values. L: organic ligand. S: surface. /31/.

The influence of humic substances on the sorption of actinides on sediments has also been demonstrated in natural systems /26, 87, 105/. As shown in Figures 50 and 51, distribution coefficients are reduced significantly in DOC-rich waters.

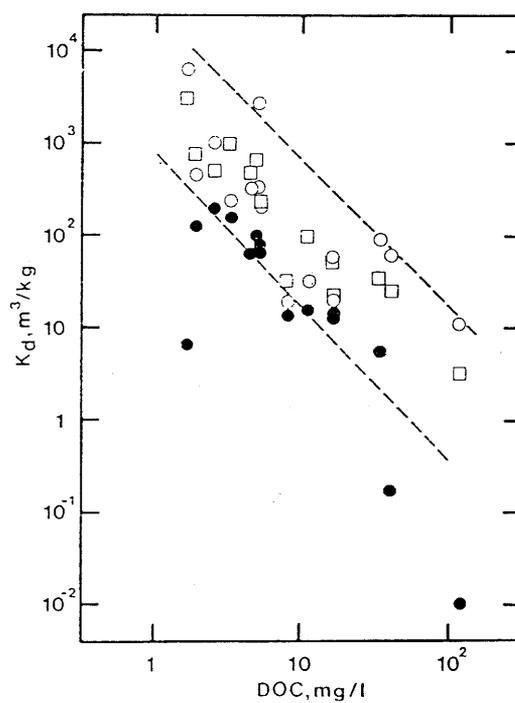


Figure 50: Variation in the distribution coefficient of Th (○), U(VI) (●) and Pu(IV) (□) between water and lacustrine sediments (0.45-35 μ m) as a function of dissolved organic carbon /26/.

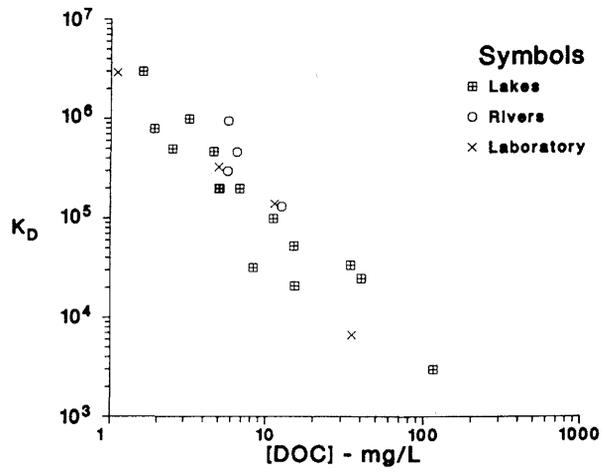


Figure 51: The distribution of plutonium(III/IV) between sediments and water as a function of dissolved organic carbon /87/. K_d in litre/kg.

7. SUMMARY AND DISCUSSION

Humic substances dissolved in natural waters are of particular interest from the point of view of their complexation properties. The fact that these substances cannot be fully characterised makes it difficult to describe their ligand behaviour quantitatively.

7.1 Humic substances

Humic substances are complex organic macromolecules containing about 50 % carbon and 40 % oxygen. They are formed in waters and soils from biodegradation products of the biomass. The dissolved components are divided into humic acids (insoluble at pH 1) and fulvic acids (soluble at pH 1). The component in soils which is insoluble in water and alkali is termed humin.

The molecular weights of fulvic acids are generally in the range 500 to 2000 daltons (D). Aquatic humic acids have higher molecular weights (typically up to 5000 D). Humic acids from soils reach molecular weights of up to 100,000 D and are present as colloids.

Humic substances are polyelectrolytes whose behaviour is determined mainly by carboxyl and phenolic OH-groups. The contents are in the order of 5 and 2 mmol/g humic material respectively.

The structure of humic substances can only be approximated using a combination of different methods. Since the raw materials from which they are formed are extremely diverse, they cannot be described as uniform compounds. Consequently, structural models are restricted to characterising the type and are incapable of reproducing the natural diversity.

Humic substances are stable over geological timescales and are therefore found in old sediments. As they alter diagenetically with time, there is a reduction in carboxyl content and further polymerisation. Both of these processes reduce solubility in water so that their influence on the solution chemistry of metals gradually decreases. However, as insoluble humin, they continue to affect the sorption properties of the rock.

Humic substance concentrations of a few ppm are common in natural waters. If the mean carboxyl content of 5 mmol/g is assumed to be equivalent to the complexation capacity, this gives a ligand concentration of 1 to 10 $\mu\text{mol/litre}$. This value is to be compared with natural heavy metal concentrations which lie in the ppb range, but also with concentrations of inorganic ligands (carbonate, phosphate, fluoride).

In sediments, the organic carbon content is in the order of 5 %, of which only a proportion is water-soluble. Pore-waters can nevertheless show a high DOC-content (e.g. 200 ppm in Belgian Boom Clay).

7.2 The protolytic behaviour of humic substances

The protolytic behaviour of humic substances is determined mainly by carboxyl and phenolic OH-groups. The acidity of the individual groups is modified by structural and electrostatic influences. In the pH range of natural waters, carboxyl groups are largely deprotonated.

The titration curves for fulvic and humic acids can be described using polyelectrolyte models (which only take account of electrostatic interactions) or by chemical mixing models.

The electrostatic models do not correlate well with structural concepts. The mixing models therefore seem to be more realistic from a chemical point of view and can model the titration curves using a selection of between three and six simple acids. The wide range of substituent influences on acidity is explained extremely elegantly by a bimodal Gaussian distribution of the pK_a values for the carboxyl and phenol groups. This model is based on the fact that the pK_a values of simple carbonic acids and phenols each give an approximative normal distribution (Fig. 21).

7.3 Humic substances as ligands

Because of the macromolecular character and structural diversity of humic substances, there appears to be little prospect of characterising their ligand properties accurately. Experimental results can only be described using very simple models, although qualitative data can be derived from structural investigations.

Humic substances of terrestrial origin contain a relatively high proportion of aromatic carbon. Phthalic acid and salicylic acid groups as well as o-diphenols will play an important role here as bidentate ligands. For aquatic humic substances with high aliphatic carbon contents, the formation of pseudochelates is possible. Hydroxycarbonic acids, ketonic acids and dicarbonic acids also come into consideration as strong ligands.

The nitrogen and sulphur contents of humic substances are low but both elements can function as extremely strong selective ligands if the steric arrangement is favourable. Porphyrin rings and hydroxamic groups should be mentioned in this context.

Conventional model concepts tend to contrast with the situation outlined here. Complexation by humic substances is usually described using an n-sites model, which assumes the formation of 1:1 complexes for all ligands (i.e. functional groups). $n \leq 3$ is generally sufficient for modelling experimental data. Each class of ligands is characterised by its concentration and by a complexation constant. Models which assume a variable stoichiometry (ML- and ML_2 complexes) do not differ significantly from the simple mixing models.

If these simple complexation models are compared with the proposed structures for humic substances, there is no doubt that they do not do justice to chemical reality. This is less true of the simple polyelectrolyte models which assume one or two types of ligand and describe complexation with intrinsic constants and electrostatic interactions.

The affinity spectra $[L] = f(\log K)$ take better account of the chemical diversity of the humic substances. Apart from the difficulties involved in integrating such models into speciation programs, relatively small experimental errors can cause serious distortions in the affinity spectrum. A simpler approach seems to be to assume a Gaussian distribution of the complexation constants and only 1:1 complexes. While the use of such a model for describing protolytic behaviour is chemically justified, a near-normal distribution of the stability constants is not confirmed.

Comparisons show that different, and to some extent contradictory, models can be applied successfully to the experimental data. One should however be aware that, although all the models are suitable for curve-fitting (because they contain enough adjustable parameters), they can only describe chemical reality in a rudimentary manner. They should not therefore be used for extrapolation beyond the concentration range covered by the experiments.

Complexation experiments do not detect strong ligands - which can be relevant for the behaviour of radionuclides in an aquatic system - if their concentration is lower than that of the minimum total metal ion concentration in the experiment. Extrapolation to lower metal ion concentrations is formally possible with the normal distribution model. Although the $[L]/\log K$ distribution of this model is not unreasonable, it is arbitrary and extrapolations on this basis would therefore be speculative.

In this situation, selecting a complexation model for humic substances becomes a matter of taste. If the economy of thought proposed by ERNST MACH is the criterion, the choice would have to be the simple mixing model.

The fact that such models can be easily integrated into speciation codes such as MINEQL and PHREEQE should not obscure the fact that published stability constants cannot be used for reliable calculations because these are formal constants which are only valid for a specific solution composition (pH, ionic strength,...). The value pairs K_i , $[L]_i$ are always determined for specific concentration ranges of metals and humic substances and are not generally applicable to any concentration ratios. A comparison of the constants used in different papers is also problematic, even if they have been determined for the same pH and ionic strength.

A particular gap in this area is the lack of a simple model for describing the influence of pH and ionic strength on complexation.

These remarks apply particularly to humic substance complexes of the actinides where constants were generally determined at low pH values. As a departure from usual practice, the experimental data are interpreted in this case on the basis of ML^- and ML_2^- complexes; the definition of the total ligand concentration also deviates from normal models.

Comparative investigations have shown that fulvic acids of differing origin do not differ significantly in their ligand behaviour towards copper. Exercising some caution, it can be deduced from this that, for experimental purposes, an easily accessible model substance can be used instead of a site-specific humic substance. A differentiation between humic and fulvic acids and according to origin (aquatic or terrestrial) would, however, appear to be advisable.

The selectivity of humic substances for divalent cations essentially follows the Irving-Williams series /42/ (p. 67). It is however possible that, at high humic substance/metal ratios, deviations from this sequence will occur if the humic substance contains a highly selective ligand for specific cations in low concentration. This aspect has to be taken into account if metals of interest are present at extremely small trace levels.

7.4 **Redox reactions of humic substances**

Humic substances can take part in irreversible and - with their quinone components - reversible redox reactions. They behave as reducing agents with respect to plutonium(VI) and neptunium(VI), but not uranium(VI).

7.5 **Sorption of humic substances on mineral phases**

Humic substances can influence the sorption of cations on mineral surfaces. They do this on the one hand by forming dissolved complexes, but also by their adsorption onto the mineral. This produces a modified surface which causes a change in sorption behaviour with respect to the metal ion. Although these complex interactions are understood in principle, there is a need for a wide range of investigations with relevant nuclides.

In natural waters, the sediment/water distribution coefficients of the actinides are lowered by humic substances. Sorption in this pH range is therefore reduced by formation of dissolved complexes.

8. CONCLUSIONS AND RECOMMENDATIONS

The influence of humic substances on the solution chemistry of fission products and actinides cannot be described quantitatively for natural systems given current knowledge. Not only specific data but also predictive models are still lacking. Given the extensive body of literature on this subject, it would appear to be presumptuous to claim that this problem will be solved in the foreseeable future. However, this is no reason for resignation: it is still possible that a pragmatic approach to the problem could provide sufficient information to allow at least a good estimation of the influence of humic substances on complexation in natural waters.

The question then arises as to whether the presence of dissolved humic substances reduces speciation calculations with inorganic ligands alone to the status of a useless exercise. For a humic substance content of 1 ppm (typical of surface waters), the complexation capacity can be roughly estimated as 5 μmol per litre. Compared with the trace concentrations of heavy metal in natural waters, this value is considerable if it is assumed that only a small percentage of the total complexation capacity is represented by strong ligands. On this basis, the influence of humic substances can only be ruled out with any certainty at extremely low concentrations (< 0.1 ppm ?). Correlations between metal concentrations and dissolved organic carbon /60/ show that DOC concentrations of 1 ppm influence the solubility of tri- and four-valent metal ions.

Discussions repeatedly raise the question whether the humic substance content of a water can be simulated for model calculations by a mixture of defined organic ligands - for example salicylic acid, phthalic acid and EDTA. The assumption of such a mixture has the advantage that the pH-dependence of the complex stability and the competition of inorganic ligands can be calculated. Such an approach seems to be attractive, at least for identifiable bidentate ligands. However, a closer inspection reveals that the procedure is unsuitable. BUFFLE has shown for a series of metal ions that humic substances form complexes which are more stable than a mixture of salicylic and phthalic acid /14/. The choice of non-selective EDTA as a model for the "hidden" strong ligands of low concentration is arbitrary, but possibly also conservative.

Before suggestions can be made for an investigation programme, it is useful to recapitulate on the gaps and weak points in work performed up till now. Complexation data in the pH range of natural waters are the main thing lacking. Because the tendency has been to select metal/humic substance concentration ratios which are unrealistically high, the contribution of strong trace ligands is overlooked. The competition for complexation of different metals is also relatively unknown territory.

These deficiencies are largely a result of experimental difficulties, which should not be underestimated. An experimental programme should therefore firstly address that which is feasible; that which is desirable should be kept in view and reached step by step.

Bearing this in mind, the following procedure is recommended:

- a) Determination of distribution coefficients: It is relatively easy to determine K_d values for a colloidal humic substance which can be separated from solution by dialysis or ultrafiltration /32, 70/. Appropriate radionuclides can be used in tracer concentrations and the influence of pH, inorganic ligands and competing cations can be investigated. Such investigations are primarily for orientation purposes. They are designed to highlight the significance of the individual parameters and can be used as a basis for planning more refined experiments (e.g. determining adsorption isotherms under specified conditions).
- b) Investigations using gel-filtration: It is not possible to separate low molecular weight fulvic acids using ultrafiltration. With the gel-filtration method /73/, however, it is possible to investigate the complexation properties of such compounds. Concentration ratios which are somewhat closer to reality can be simulated by using suitable pH- and metal ion buffers.
- c) Analogue studies: As mentioned in section 4.11, information on the relative influence of organic material can be derived from correlations between humic substance content and trace metal concentrations in the water. When planning large-scale water analysis programmes at potential disposal sites, such investigations should be included. An attempt should be made to link these correlation studies as closely as possible to the " K_d programme".

An ideal situation would be to have site-specific humic substances available for experiments. However, the isolation of large quantities of humic substances is expensive and, to begin with, it is acceptable to use commercially produced materials (e.g. colloidal humic acid and aquatic fulvic acid). The extent to which the results can then be transferred to site-specific material can then be checked at a later date. Isolation and characterisation of site material should be entrusted to a specialised group with relevant experience.

The final point to be discussed is the extent to which these humic substances require to be characterised. It is certainly necessary to determine distribution of molecular weight, carboxyl and phenol acidity and, possibly, the aromatic component. The large expense involved in more detailed structural characterisation (which would also have to take account of the highly selective trace donor groups) does not appear to be justified until complexation can be described by advanced models which can take structural data into account.

9. ACKNOWLEDGEMENTS

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