

Chapter VI

Metal Ion Binding by Humic Substances

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VI.1. Introduction

Ionic interactions in natural waters are significantly influenced by the presence of natural organic acids which constitute a mixture of different molecules with varying size, containing different functional groups [82STE]. The present methods of extraction are used to divide these natural organic acids into two major categories; hydrophobic and hydrophilic acids. The terms hydrophobic or hydrophilic are defined by adsorption or non adsorption onto XAD-8 amberlite resins, respectively [81THU/MAL, 91MAL, 92PET]. Recent advances have shown that the hydrophobic properties increase with a decrease in pH while their hydrophilic properties increase with an increase in pH [85AIK/MCK, 89EPH/BOR]. Molecular size variations and their correlations with other parameters, *i.e.*, acidity, fluorescence, and turbidity have prompted researchers to postulate that these substances have fractal properties [94OST/MOR, 94SEN]. The solution chemistry of these organic acids, though not well understood, has aroused the interest of many researchers, *e.g.* [70GAM, 80GAM/UND, 80PER/REU, 85MAR, 86EPH/ALE, 92BAR/CAB]. Complicating factors influencing their solution chemistry have been identified as the functional group heterogeneity and the heterogeneity in the molecular size and shape leading to ionic strength effects [86EPH/ALE, 90WIT/RIE, 92TIP/HUR, 93WIT/RIE, 95EPH/PET].

The role that natural organic acids may play in the distribution and mobility of the trace metal ions in surface and ground water systems can be anticipated by examining their interactions with metal ions in the presence and absence of solid/particulates of

geologic origin [93EPH/ALL]. Fulvic and humic acids are normally used to represent natural organic acids in laboratory studies [78SCH, 79PER], as a complement to field studies. These acids which are hydrophobic at lower pH (~ 1) are the predominant species among the natural organic acids which sequester metal ions in solution [94BUR].

In this Chapter, the definition of natural organic acids (with emphasis on humic and fulvic acids), their isolation and characterisation methods, their interaction with metals, their redox properties and the methods of data acquisition and analyses will be presented. Additionally, implications with regard to nuclear waste management and recommendations will be provided.

VI.2. General overview

Humic and fulvic acids are defined as “a class of ubiquitous, biogenic, heterogeneous organic acids which do not belong to a known class of compounds” [82STE]. An intrinsic problem with this definition is the lack of uniqueness. It must be emphasised that the characteristics of any humic or fulvic acid sample depend primarily on the method of isolation/extraction.

These substances contain both Brønsted (proton-donating) and functional groups composed of hydrogen-bonding moieties, *e.g.*, carbohydrates [90PER/GJE]. The genesis of humic substances is envisaged to include processes like microbiological metabolism, mineralization, abiotic oxidation, photochemical processes, adsorption, precipitation and re-polymerization [90PER/GJE].

In an attempt to promote inter-laboratory checks and collaboration, the International Humic Substances Society (IHSS) in 1983 adopted a standardized method of isolation/extraction of humic substances [85AIK/MCK]. However, a number of other methods of isolation are also described in the literature. Irrespective of the isolation methods, humic and fulvic acids seem to have certain general characteristics, *i.e.*, the presence of oxygen-containing functional groups, *e.g.*, $-\text{COOH}$, phenolic and enolic $-\text{OH}$, quinones and semi-hydroquinones, nitrogen-containing functional groups, $-\text{RNH}_2$, and sulphur-containing functional groups, $-\text{RSH}$. The presence of these functional groups is responsible for their high affinity for metal ions and other trace components in the environment [82STE].

The concentrations of humic substances in surface and ground waters depend on the concentration of total organic acid, TOC, which may be divided into particulate form and dissolved organic carbon, DOC. The separation of particulates from the dissolved organic carbon has normally been effected using filters with an arbitrary cut-off of 0.45 micron. The DOC in surface waters in the US has an average of $5 \text{ mg C} \cdot \text{l}^{-1}$ ranging from 1.5 to $10 \text{ mg C} \cdot \text{l}^{-1}$ [91MAL] with approximately 50% of humic substances. The DOC in groundwaters have concentrations ranging from 2 to $4 \text{ mg C} \cdot \text{l}^{-1}$. A generalization of these data is that the concentration of humic substances in aquatic environments range from $20 \mu\text{g} \cdot \text{l}^{-1}$ in groundwaters to $30 \text{ mg} \cdot \text{l}^{-1}$ in surface waters [81THU/MAL].

VI.2.1. Isolation and extraction of humic substances

The primary objective of any isolation/extraction procedure is to obtain a sample which is identical to the original material. The isolation is made to facilitate the laboratory studies needed to obtain information about the material and to understand and predict its behaviour in the environment. Various methods of isolation of humic substances in both aquatic and terrestrial environments have been developed to obtain samples that are free from contaminants, mainly metal-ions [81THU/MAL, 83MIL/TUS, 83PLE/JOS, 87GRE/POW, 91MAL, 92PET, 94PET/EPH]. However, there is a school which believes that the samples obtained by the various isolation methods may be chemically different from the non-isolated material. Hence, their studies of natural organic acids have utilised samples which have not been extracted [91MAE/ELE].

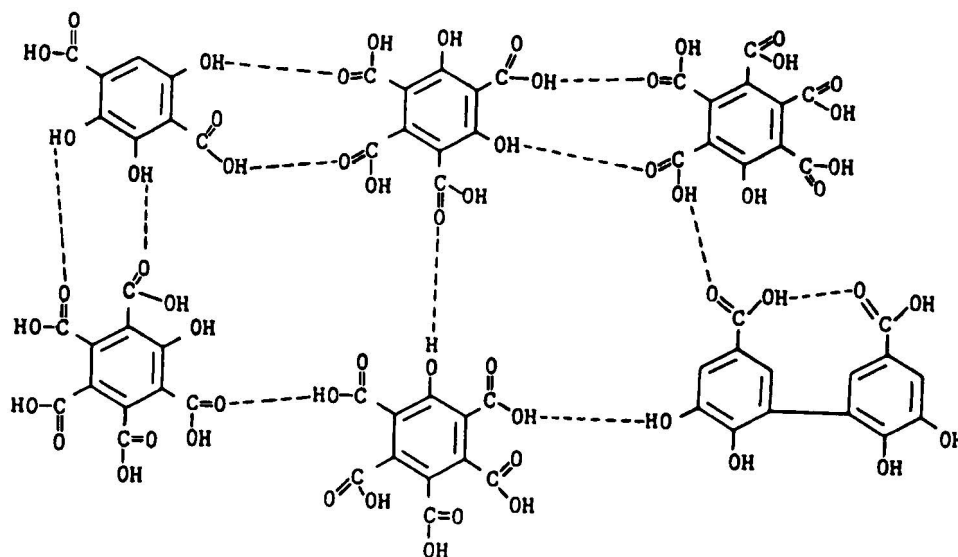
The isolation/extraction procedures are slightly different for material from terrestrial and aquatic environments. In the terrestrial environment, the procedure commonly used is alkali extraction [82STE]. In aquatic systems, the isolation consists of obtaining the hydrophobic and hydrophilic portions of the dissolved organic carbon (DOC) and determining the fractions which are acidic, basic and neutral, respectively. The method adopted by the IHSS, *i.e.*, the XAD-8 method, seems to be widely used by researchers [81THU/MAL]. However, a draw-back of this method is that it requires the addition of HCl to the water samples in order to reduce the pH, to render the fulvic and humic acids hydrophobic (so they can adsorb on XAD-8). Addition of HCl has been avoided in an alternative method where diethylaminoethyl (DEAE) cellulose has been employed to isolate the organic acids at their natural pH, before subsequent adsorption on XAD-8 resins [92PET]. There are arguments as to the similarity of the samples obtained from direct addition of HCl cum XAD-8 adsorption and DEAE cellulose cum XAD-8 adsorption methods. However, comparisons of humic substances extracted from various origins with different methods seem to indicate that these substances have much in common [94PET/EPH]. Another method of isolation of humic substances from aquatic environments involves the successive ultrafiltration of water sample through membranes of varying cutoff sizes, *i.e.*, 100 000, 10 000 and 1 000 daltons ¹ [91PEU/PIH].

VI.2.2. Characterisation methods

Humic and fulvic acids are characterised by using various analytical methods, such as elemental analysis, NMR, FTIR, UV-visible, *etc.* A considerable number of analytical methods have been employed in efforts to obtain a complete structure for fulvic and humic acids. These physicochemical methods also include ultracentrifugation, viscosity, colligative property measurements, light scattering techniques, gel chromatography and electrophoresis [89HAY/MCC]. Despite the advances in the state-of-the-art, structures for humic and fulvic acid have not been obtained. By using information on the reactive functional groups, elemental analysis potentiometric titration results and other chemical analyses [72SCH/KHA] together with known restrictions on the conformation, it is

¹ One "dalton" is one atomic mass unit: conversion factor to grams is 1.66024×10^{-24} .

Figure VI.1: Structure of fulvic acid as proposed by Schnitzer and Kahn. Reprinted with permission from [72SCH/KHA].



possible to deduce reasonable structure models for humic/fulvic acids (see Figure VI.1).

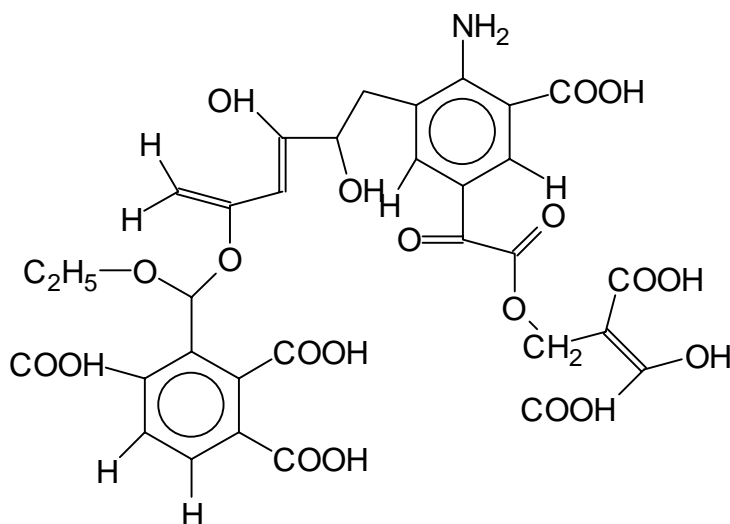
Such an exercise has been performed for an aquatic fulvic acid [89EPH/BOR] and the postulated structure for the fulvic acid shown in Figure VI.2 is not very different from those proposed by earlier researchers [60FLA, 66KON, 72SCH/KHA, 83HAR/BOR]. The extent of aromaticity is much lower, reflecting the origin of the fulvic acid from an aquatic environment.

Isolation of humic substances from aquatic environments normally yield small quantities of material, thus the selection of characterisation method is of vital importance. The criteria for the selection should be the attainment of maximum information through the employment of a minimum amount of sample. In a recent attempt, UV-visible, elemental analysis, total organic acid, potentiometric titrations and molecular weight determinations were considered an appropriate combination for the realisation of this requirement [94PET/EPH]. In such an exercise, it was concluded that fulvic acids extracted from different origins have large similarities.

Information obtained from the application of the various physicochemical analytical methods may be summarised as follows:

1. Humic substances are acidic and their acidity is primarily due to $-\text{COOH}$ and phenolic or enolic $-\text{OH}$ functional groups [70RAS/KIN, 78SCH, 80PER/REU, 80SAI/HAY]. Numerous attempts have been made to differentiate between the $-\text{COOH}$ and $-\text{OH}$ groups [82STE]. However, the most important parameter determining their properties in the aquatic environment is the total titratable acidity (which may or may not be a combination of the $-\text{COOH}$ and $-\text{OH}$) [70GAM, 72GAM,

Figure VI.2: Hypothetical structure of Bersbo aquatic fulvic acid based on elemental analysis and potentiometric titrations in aqueous and non-aqueous media.



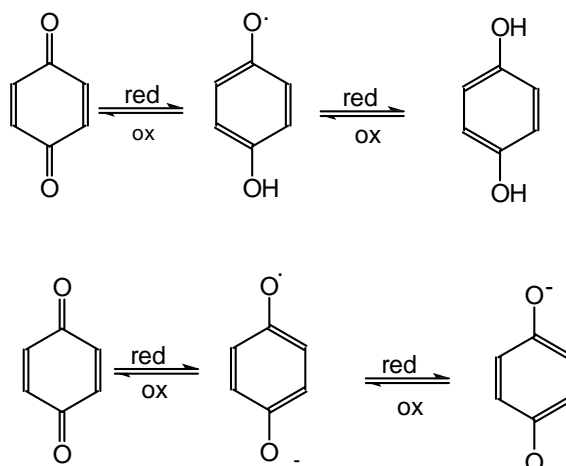
73GAM/SCH, 78PER, 79PER, 80PER/REU, 82GIL/RIL, 82STE, 83PER/LYT]. The titratable acidity is considered to be the value which the humic substance will exhibit under normal environmental conditions [86EPH/ALE]. This does not presuppose that only the titratable acidity will be involved in the complexation with trace metals and other low-molecular weight species. For 14 aquatic fulvic acid samples isolated from a variety of geographical locations (Sweden, Canada, Germany, USA) an average titratable acid capacity of $5.1 \text{ meq} \cdot \text{g}^{-1}$ of sample was obtained [91PET]. The range of acidity was 3.3 to $9.86 \text{ meq} \cdot \text{g}^{-1}$. These results are significantly lower than the corresponding values quoted for soil fulvic acids, where the average is $8.2 \text{ meq} \cdot \text{g}^{-1}$ and the range from 6.4 to $14.2 \text{ meq} \cdot \text{g}^{-1}$ [82STE].

- Fulvic acids are smaller than typical polyelectrolytes, *e.g.*, poly-metacrylic acid, PMA [67TAN], and heterogeneous with respect to molecular size [69HAN/SCH]. The average molecular weight, M_n , for a number of aquatic fulvic acids is 1153 ± 376 daltons with a range from 660 to 1750 daltons [94PET/EPH]. These molecular weight distributions were determined via the use of gel filtration chromatography, which is normally considered to give higher values than the vapour pressure osmometric measurements [69HAN/SCH, 90MAR/RED]. The average value of M_n (1153 daltons) compares well with other reported values for fulvic acids [82STE, 85AIK/MCK]. The number-average molecular weight, M_n , is expressed as:

$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$

where n_i is the number of molecules with molecular weight M_i . The weight-average

Figure VI.3: One-electron step reactions rationalising the redox properties of humic substances (Adapted from [90SEN]).



molecular weight, M_w , is correspondingly expressed as:

$$M_w = \frac{\sum w_i M_i}{\sum w_i}$$

where w_i is the total weight of molecules with molecular weight M_i . The ratio of M_w/M_n is equal to 1 for monodisperse materials and $M_w/M_n > 1$ for polydisperse substances [72SCH/KHA, 82STE, 94PET/EPH].

VI.2.3. Redox properties of humic substances

Humic substances have been observed to reduce oxidised forms of certain metal ions, examples of which are Fe(III) to Fe(II), Hg(II) to Hg(0), V(V) to V(IV) and also I_2 and I_3^- to I^- [81SKO/WIL, 84WAI/MOR]. From E_H/pH measurements, the following half-cell reaction for a particular fulvic acid was suggested:



with a potential of ~ 0.5 V (*vs.* NHE) [81SKO/WIL]. This potential will differ for different fulvic acid samples. The redox properties of humic substances have been attributed to the presence of phenols, quinones and semi-hydroquinones in the humic molecule and has been rationalised by one-electron redox reaction in solution as shown in Figure VI.3.

The redox properties of humic substances have been studied using EPR, ESR and Mössbauer spectroscopy [77SEN/CHE, 87GOO/CHE]. The oxidation of humic substances is very rapid as indicated by redox titrations with iodine and by photometric detection of the reaction with potassium ferricyanide [91MAT2]. The reaction was found to be complete within 48 hours.

VI.3. Solution chemistry of humic substances

The solution chemistry of these natural organic acids is not fully understood even though considerable advances have been made over the past decade. This short-coming is a consequence of a combination of factors, such as:

- the absence of a unique structure of humic substances,
- the variation in the methods of isolation and extraction,
- the absence of specific analytical methods suitable only for humic substances.

The complex nature of these compounds has made it necessary to develop simplified models to describe them and their chemical properties. The first problem with modelling lies with the manner in which they may be conceptualised. A study of the literature reveals the following examples:

1. Strongly associated aggregates of acids, each of comparatively low molecular weight [86WER].
2. An assemblage of identical “mean fulvic acid” units; a fulvic acid unit is a hypothetical macromolecule that contains one or more distinct classes of acidic functional groups [77SPO/HOL].
3. An oligoelectrolyte (intermediate between simple ions and true polyelectrolytes) composed of impenetrable charged spheres [92BAR/CAB].
4. An assemblage of relatively small amphiphilic moieties which are slightly different but composed of four to five predominant separate acidic sites, with each site characterised by a distribution of acidity constants round an average value [91EPH/RED].

VI.3.1. Proton interactions with humic substances

The concepts enumerated in previous section have led to the development of two major types of models, namely the discrete ligand approach and the continuous distribution approach.

VI.3.1.1. Discrete ligand models

In the discrete ligand approach, the observed protolytic and metal binding behaviour has been attributed to a limited number of predominant sites. Additionally, an electrostatic term has normally been employed to estimate the deviation from ideality in the polyelectrolyte as a result of the change in the electrostatic free energy of the macromolecule caused by group-group interaction accompanying the ionization process. A literature survey reveals that four sites are normally employed to account for the observed acid-base properties [77SPO/HOL, 86EPH/ALE, 88GRE/POW, 89EPH/BOR, 89EPH/BOR2]. However,

a number of researchers have employed three sites [88TIP/BAC, 90TIP/RED, 91FAL]. Five sites [89EPH/BOR] and six sites [85PAX/WED, 91PAX/WED] have also been used to describe the observed potentiometric behaviour of fulvic acids. The absence of a comprehensive method for estimating site-to-site interactions has resulted in their exclusion from the discrete ligand approach. In the school of discrete ligand approach, there exists subtle differences in the method of estimating the electrostatic effects, and the number of sites necessary to describe experimental results. Examples of the discrete ligand models used in the literature are given below.

VI.3.1.1.1. Tipping's model V

Ion binding by humic substances, which is described in terms of complexation at discrete sites, is postulated to be modified by electrostatic attraction and/or repulsion and non-specific binding due to counterion accumulation [92TIP/HUR, 93TIP]. In the model, variations in apparent binding strengths of the major proton-dissociating groups ($-\text{COOH}$, phenolic $-\text{OH}$) are described by using an electrostatic model involving a negative framework and counter-ions. Eight proton-dissociating sites are envisaged and the metal binding is postulated to occur either at a single proton-dissociating site (monodentate) or in a bidentate fashion. Electrostatic corrections are made using the expression e^{2wzZ} , where z is the charge on the cation, Z is the net charge on the humic framework, w is the electrostatic interaction factor obtained from the following:

$$w = P \log_{10} I$$

where I is the ionic strength, and P is an adjustable parameter [93TIP]. Additional counterion concentrations in the diffuse layer of the humic molecule are calculated using Donnan expressions [93MAR] with the volume of the diffuse layer, V_D calculated by:

$$V_D = \left(10^{-3} \frac{4\pi N_A}{3 M_w}\right) \left[\left(r + \frac{1}{K_{\text{DH}}}\right)^3 - r^3 \right]$$

where N_A is Avogadro's number, M_w is the humic molecular weight, r is the radius of the humic molecule, and K_{DH} a Debye-Hückel parameter which depends on the ionic strength and is a measure of the diffuse layer. The humic molecule is considered as a rigid sphere to permit the application of the Debye-Hückel model.

Tipping's model V contains seven adjustable parameters for fitting proton dissociation and two parameters additionally for each cation that can bind at the acid-dissociating sites [92TIP/HUR, 93TIP].

VI.3.1.1.2. The oligoelectrolyte model

In the recent oligoelectrolyte model [92BAR/CAB], humic substances are again represented as impenetrable spheres and the electrostatic effect is calculated using approximations of the nonlinear Poisson-Boltzmann equation. The "local" concentration of metal

ion near the charged polyions, $[M^{z+}]_{loc}$, is related to the concentration of the metal ion in the bulk solution, $[M^{z+}]$, as follows:

$$[M^{z+}]_{loc} = \lambda^z [M^{z+}]$$

where the electrostatic factor, λ , is given by:

$$\lambda = \exp\left(\frac{-F\Psi_0}{RT}\right) \quad (VI.1)$$

where Ψ_0 is the electrostatic potential at the surface of the sphere, F is Faraday's constant, R is the universal gas constant and T the absolute temperature. The electrostatic factor can also be interpreted as a ratio of polyion activities when the aqueous components are diffusible into the polymer network, just as in the case of Donnan equilibrium [93MAR]. The model consists of a total of 14 parameters which may be reduced to 9 [92BAR/CAB]. This model was successfully employed to explain pH and copper titration data by considering two copper binding sites and an additional acidic site. The authors claim that the model is simplistic and minimises the number of arbitrary fitting parameters. That much emphasis is placed on just data-fitting is a disadvantage of the model.

VI.3.1.1.3. The Gibbs-Donnan polyelectrolyte two phase model

New advances in the description of proton and metal ion binding by humic substances have been made by the adaptation of an approach originally designed for synthetic polyelectrolytes to humic substances [84MAR/RED, 84MAR/RED2, 85MAR, 88MAR/RED, 93MAR]. The approach which is based on the Gibbs-Donnan equilibrium fits into the discrete model category.

In typical polyelectrolyte solutions, the intrinsic microscopic acid dissociation constant of the repeating functional group HA is defined by:

$$K_a^{intr} = a_{H^+(surf)} \left(\frac{\alpha}{1-\alpha}\right) \quad (VI.2)$$

where $a_{H^+(surf)}$ represents the activity of the hydrogen ions at the charged surface of the polyelectrolyte while α , the degree of neutralization, is an experimental quantity. The activity of the hydrogen ion in the bulk solution a_{H^+} , the other experimental quantity, is related to $a_{H^+(surf)}$ by the Boltzman expression:

$$a_{H^+(surf)} = a_{H^+} e^{-F\Psi/RT} \quad (VI.3)$$

where Ψ is the difference in potential between the charged polymer surface and the bulk of the solution, F is Faraday's constant, R is the universal gas constant and T is the absolute temperature. Incorporation of Eq. (VI.3) into Eq. (VI.2) gives the following equation²:

$$pK_a^{intr} = pK_a^{app} + (0.434 F\Psi/RT) \quad (VI.4)$$

² In this Chapter the "p" nomenclature is widely used: pK , pH , pM , *etc.*, are symbols for $-\log_{10} K$, $-\log_{10} a_{H^+}$, $-\log_{10} a_M$, *etc.*

where pK_a^{app} is defined as $\text{pH} - \log_{10}[\alpha/(1 - \alpha)]$.

Thus for typical polyelectrolytes, a plot of pK_a^{app} versus α extrapolated to $\alpha = 0$ (Ψ approaches zero as α approaches zero) for any ionic strength gives the intrinsic constant, pK_a^{intr} . The effect of ionic strength upon such a plot comes from its influence upon the value of Ψ as α is varied. With crosslinked polyelectrolytes (gels), the pH inside the gel is not accessible to direct measurements. Hence, a study of the polyelectrolyte properties of weakly acidic gels has to be based upon the pH of the external solution phase in equilibrium with the gel phase. These properties have been observed to be a sensitive function of the water content of the gel (which depends on the flexibility of its matrix) and the ionic strength of the aqueous medium. At equilibrium, during each step of the potentiometric titration of a weakly acidic polymer gel, HA, in the presence of a simple background electrolyte, MX, the chemical potential, μ , of the *diffusible* components, HX, MX and H₂O are equal in both phases:

$$\begin{aligned}\mu_{\text{HX(aq)}} &= \mu_{\text{HX(gel)}} \\ \mu_{\text{MX(aq)}} &= \mu_{\text{MX(gel)}} \\ \mu_{\text{H}_2\text{O(aq)}} &= \mu_{\text{H}_2\text{O(gel)}}\end{aligned}$$

where “aq” and “gel” identify respectively the aqueous solution and the gel phases. By assuming that the chemical potential in isothermal systems may be divided into two terms, one of which depends only on the composition and the other on pressure, the μ of each component i ($i = \text{HX}, \text{MX}, \text{H}_2\text{O}$) in a solution of ionic strength $I = [\text{MX}]$ and under a pressure p is given by

$$\mu_i(p, I) = \mu_i(p^\circ, I) + (p - p^\circ)V_i \quad (\text{VI.5})$$

where p° is the standard pressure, 1 bar, and V_i is the partial molar volume of component i . V_i might be assumed to be independent of composition and pressure without introduction of significant error. The activity, a_i , of the i^{th} component is defined by

$$\mu_i(p^\circ, I) = \mu_i^\circ(p^\circ) + RT \ln a_i \quad (\text{VI.6})$$

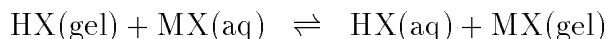
where μ_i is the chemical potential of the i^{th} component in the standard state. Combination of Eqs. (VI.5) and (VI.6) yield the following:

$$\mu_i(p, I) = \mu_i^\circ(p^\circ) + RT \ln a_i + (p - p^\circ)V_i \quad (\text{VI.7})$$

The chemical potentials of MX and HX in each phase are thus given by

$$\begin{aligned}\mu_{\text{HX(aq)}} &= \mu_{\text{HX(aq)}}^\circ + RT \ln a_{\text{HX(aq)}} + (p - p^\circ)V_{\text{HX(aq)}} \\ \mu_{\text{HX(gel)}} &= \mu_{\text{HX(gel)}}^\circ + RT \ln a_{\text{HX(gel)}} + (p - p^\circ)V_{\text{HX(gel)}} \\ \mu_{\text{MX(aq)}} &= \mu_{\text{MX(aq)}}^\circ + RT \ln a_{\text{MX(aq)}} + (p - p^\circ)V_{\text{MX(aq)}} \\ \mu_{\text{MX(gel)}} &= \mu_{\text{MX(gel)}}^\circ + RT \ln a_{\text{MX(gel)}} + (p - p^\circ)V_{\text{MX(gel)}}\end{aligned}$$

For the system described above, the equilibrium expression for the reaction



is

$$\begin{aligned} RT \ln \left[\frac{a_{\text{HX}(\text{aq})} a_{\text{MX}(\text{gel})}}{a_{\text{HX}(\text{gel})} a_{\text{MX}(\text{aq})}} \right] + \Pi (V_{\text{MX}(\text{aq})} - V_{\text{HX}(\text{aq})}) \\ = \mu_{\text{HX}(\text{gel})}^{\circ} + \mu_{\text{MX}(\text{aq})}^{\circ} - \mu_{\text{HX}(\text{aq})}^{\circ} - \mu_{\text{MX}(\text{gel})}^{\circ} \end{aligned} \quad (\text{VI.8})$$

where Π is the osmotic coefficient, which is equal to $(p - p^{\circ})$ as expressed in Eq. (VI.7).

By choosing the same standard state in the gel and solution phases for the reacting components, the sum on the right hand side of Eq. (VI.8) is zero, and assuming that the $\Pi (V_{\text{MX}(\text{aq})} - V_{\text{HX}(\text{aq})})$ term is small enough to neglect, the following expression is obtained:

$$\ln \left[\frac{a_{\text{HX}(\text{aq})} a_{\text{MX}(\text{gel})}}{a_{\text{HX}(\text{gel})} a_{\text{MX}(\text{aq})}} \right] \approx 0$$

By the substitution of the product of single ion activities, this equation may be expressed:

$$\frac{a_{\text{H}^+} a_{\text{X}^-} a_{\text{M}^+(\text{gel})} a_{\text{X}^-(\text{gel})}}{a_{\text{H}^+(\text{gel})} a_{\text{X}^-(\text{gel})} a_{\text{M}^+} a_{\text{X}^-}} = 1$$

where cancellation of activities yields the following:

$$\text{pM} - \text{pH} = \text{pM}_{(\text{gel})} - \text{pH}_{(\text{gel})} \quad (\text{VI.9})$$

The value of pM and pH are experimentally measurable or calculable in these systems; the concentration of M^+ in the gel phase, $\text{pM}_{(\text{gel})}$, is also accessible since to preserve electroneutrality in the gel during neutralization with standard base, the concentration of M^+ must be at least equal to the concentration of the deprotonated form of the gel, $[\text{A}^-(\text{gel})]$ (except for the relatively very small quantity of $\text{H}^+(\text{gel})$ present). The concentration of A^- (the deprotonated form of the gel) is calculable from the stoichiometry of the neutralization reaction and the measured volume, V_g , of the gel,³ while $[\text{MX}(\text{gel})]$ can either be determined experimentally or estimated with the following equation:

$$([\text{MX}(\text{gel})] + [\text{A}^-]) [\text{MX}(\text{gel})] \approx [\text{MX}]^2 \quad (\text{VI.10})$$

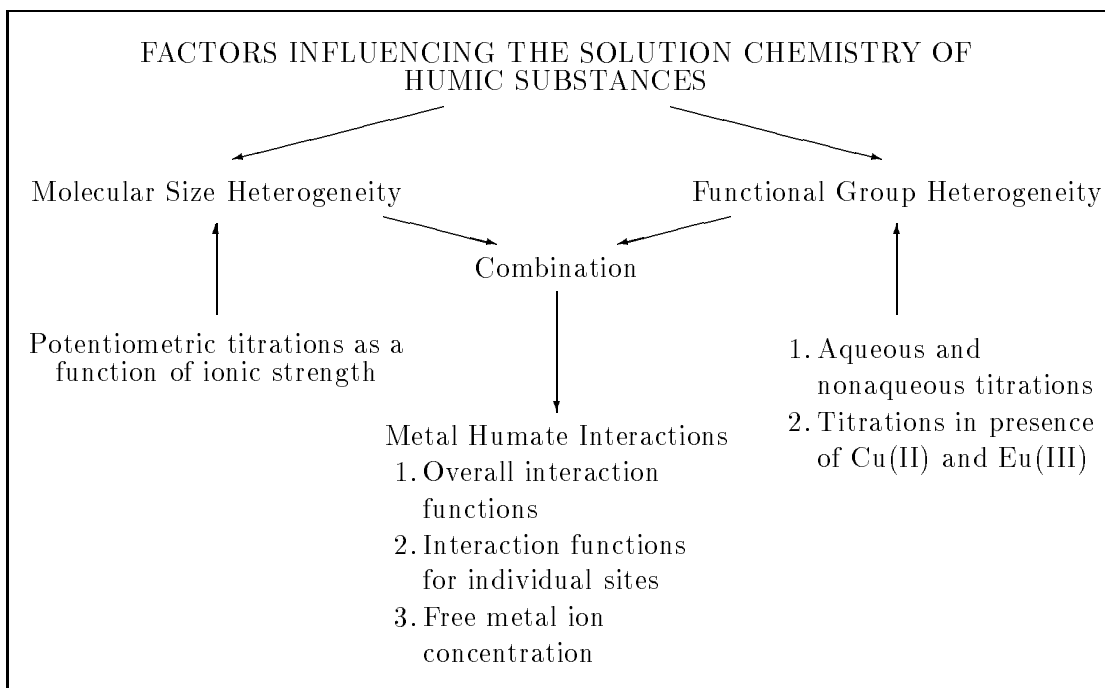
Incorporation of Eq. (VI.9) into the Henderson-Hasselbach equation ($\text{p}K_a = \text{pH} - \log_{10}\{\alpha/(1 - \alpha)\}$) yields:

$$\text{p}K_a^{\text{app}} - \text{p}K_a^{\text{intr}} = \text{pM} - \text{pM}_{(\text{gel})}$$

where $\text{p}K_a^{\text{app}}$ is the negative logarithm of the apparent dissociation constant of the weak acid repeated in the polyelectrolyte and $\text{p}K_a^{\text{intr}}$ corresponds to its intrinsic (thermodynamic) constant. The difference between polyelectrolyte gels and their linear analogs is

³ All concentrations in the gel phase have units of: $\text{mol} \cdot (\text{l of gel})^{-1}$.

Figure VI.4: Stages of the Gibbs-Donnan based program as adapted to metal-humate systems.



due to a difference in charge distribution. The separate well-defined phases of the gel-salt systems are electroneutral, the counterion enriched domain and the solution external to it in the linear analogs are not. The negative charge due to the fractional release of counterions from the polyelectrolyte domain is balanced by the equal positive charge they produce in the aqueous solution phase [88MAR/RED].

An important advantage of the Gibbs-Donnan two phase model derives from the capability it provides for separating the perturbations due to ionic strength effects and functional group heterogeneity [86EPH/ALE, 89EPH/BOR]. Figure VI.4 shows the various stages of the program used in the application of this approach to metal-humate systems [91EPH/RED].

In the literature, humic substances are normally considered as spheres or cylinders [90WIT/RIE, 92BAR/CAB, 92TIP/HUR, 93WIT/RIE, 93WIT/RIE2], but such *a priori* assumptions are avoided in this model. Instead, experimental data (aqueous titrations as a function of ionic strength) are used to obtain insight into the configuration of the humic substances in solution.

In the discrete ligand models, attempts are made to correct for perturbations of the measured concentrations of counterions, *e.g.*, H^+ and M^{z+} , by using the electrostatic term, $\exp(-F\Psi/RT)$. Such electrostatic terms are normally calculated by assuming that the humic substances are spherical to allow the use of the proper form of the Boltz-

man distribution [90WIT/RIE, 92BAR/CAB, 92TIP/HUR, 93WIT/RIE]. However, in the Gibbs-Donnan model, this term which is expressed as a counterion concentration term, is determined experimentally [86EPH/ALE, 89EPH/BOR, 91EPH/RED]. In the adaptation of the Gibbs-Donnan model to humic substances the chemistry of the humic substance as a ligand is emphasized. The stages of the approach are presented in the following paragraphs.

Based on the assumption that humic substances are composed of four to five separate acidic moieties, the potentiometric titrations are interpreted at the ionic strength where separate phase effects are minimal. The steps involved in assigning $pK_{a,i}$ values to the envisaged acidic moieties are presented below:

1. Four to five “average” sites and their respective abundances are estimated from nonaqueous titrations and titrations in presence of increasing amounts of Cu(II) and Eu(III) or La(III).
2. Initial guesses of their $pK_{a,i}$ values are made.
3. The degree of neutralization of each of the envisaged “average” sites, α_i , is computed using the following equation:

$$\alpha_i = \left(1 + 10^{(pK_{a,i} - pH)}\right)^{-1} \quad (\text{VI.11})$$

for the “critical” bulk electrolyte concentration. The “critical” bulk electrolyte concentration is the concentration after which no ionic strength effects are observed on the pK_a vs. degree of neutralization, α curve (determined to be $I = 1.00$ M) [86EPH/ALE].

4. Steps 1 and 2 above are changed until the following relationship is achieved:

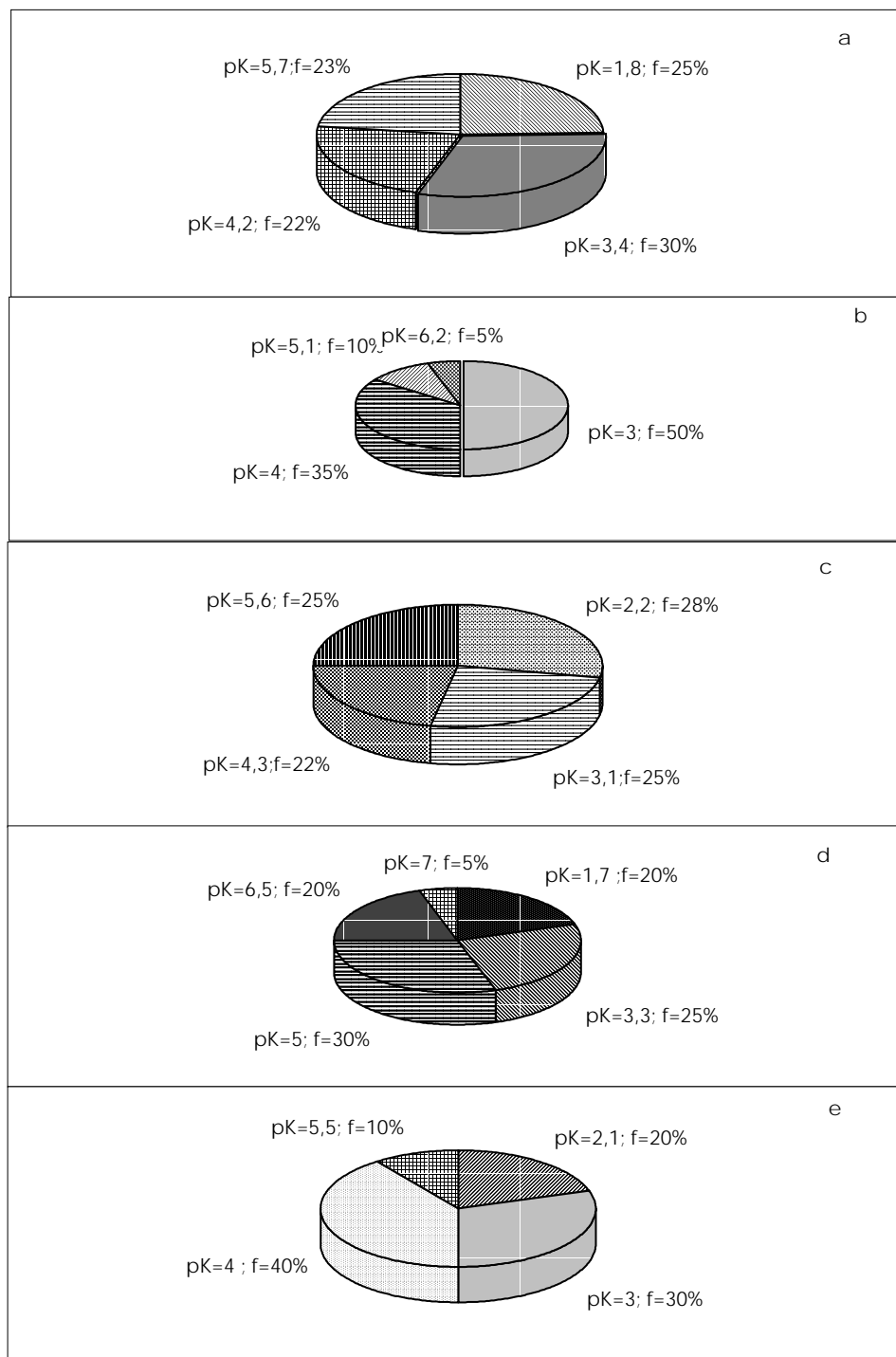
$$\sum(\alpha_i f_i) \cong \alpha_{\text{computed}} \cong \alpha_{\text{experimental}} \quad (\text{VI.12})$$

or the residual $|\alpha_{\text{computed}} - \alpha_{\text{experimental}}|^2$ reaches a minimum for the set of data points. In Eq. (VI.12), α_i is the degree of ionization for each acid site, f_i is the fraction of the total acid capacity due to the i^{th} site (determined in aqueous titrations), α_{computed} and $\alpha_{\text{experimental}}$ are the overall computed and experimental degree of neutralization, respectively [86EPH/ALE, 89EPH/BOR].

Details of the application of this model to the description of the solution chemistry of humic substances are presented elsewhere [86EPH/ALE, 89EPH/BOR, 95EPH/PET]. Examples of site heterogeneity assignments to a number of fulvic acid samples achieved by the application of the Gibbs-Donnan model are shown in Figure VI.5, where it is apparent that a large fraction of fulvic acids have a pK_a^{app} values under 4.0 suggesting $-\text{COOH}$ functionality which is corroborated by the good agreement between aqueous acid capacity and the $-\text{COOH}$ capacity in non-aqueous titrations [95EPH/PET]. The assignment of site heterogeneity facilitates the design of experimental methods with the aim of elucidating the functionality spectrum in the humic substance molecule [89EPH/BOR2, 92ARS/BOR].

Metal Ion Binding by Humic Substances

Figure VI.5: Site heterogeneity assignments to a number of fulvic acid (FA) samples, f =percentage of each acid site: *a* = Armadale FA [86EPH/ALE]; *b* = Fanay-Augères FA [94PET/EPH]; *c* = Suwanee River FA [91EPH/RED]; *d* = Bersbo FA [89EPH/BOR]; and *e* = Finnsjön FA [89EPH/BOR2].



VI.3.1.1.4. *An example of the Gibbs-Donnan Approach to Humic Substance Systems*

In all of the models employed to describe proton and metal ion binding to humic substances, the need to make electrostatic corrections to the measured experimental parameters, H^+ , M^{z+} , are of utmost importance. For the proton, this correction term is obtained by the relationships in Eqs. (VI.1), (VI.3), and (VI.4).

The assumption in the Gibbs-Donnan approach is that with subsequent increase in ionic strength, I , the electrostatic contribution to the pK_{app} term decreases until I reaches a "critical value" where further increase in I has no effect on the pK_{app} ($I \geq 1.0$ M). In the Gibbs-Donnan approach, the electrostatic term is designated ΔpK defined as:

$$\Delta pK = pK_{app} - pK_{intr} = (-0.434 F\Psi/RT)$$

An example of the approach as employed to Laurentide fulvic acid [95MAT/EPH] is shown in Figs. VI.6 and VI.7. In Fig. VI.6, the pK_{app} vs. the degree of neutralization is shown for the five different ionic strength ($I = 0.001, 0.01, 0.10, 1.0, 5.0$ M). Note that the curves for $I = 1.0$ and 5.0 M are superimposed indicating that the critical ionic strength has been reached. In Fig. VI.7, the electrostatic term (designated ΔpK) as defined in the above equation, is shown as a function of degree of neutralization for the three ionic strengths, $0.001, 0.01$ and 0.10 M.

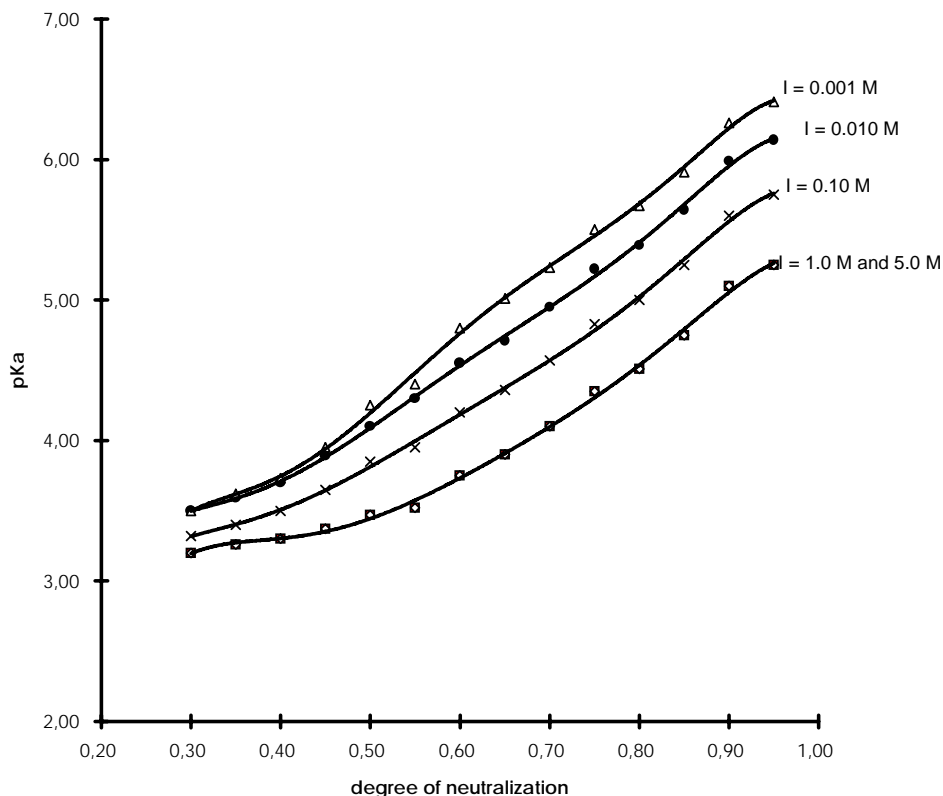
The heterogeneity factor obtained from non-aqueous titrations and titrations in the presence of Cu(II) and La(III)/Eu(III) is thus employed in conjunction with Eqs. (VI.11) and (VI.12) to obtain the predominant acidic moieties in the humic substance. An example of the exercise as applied to the Laurentide fulvic acid [95MAT/EPH] is shown in Table VI.1.

VI.3.1.2. *Continuous distribution models*

In the continuous distribution model, the properties of the various sites are assumed to overlap, thus justifying the use of statistical methods for their estimation. Variations of these models, discussed in Chapter V are presented briefly below.

- *The affinity distribution model* [83SHU/COL, 87BUF/ALT, 90WIT/RIE, 93WIT/RIE, 93WIT/RIE2]. In the application of the continuous distribution model to the acid-base properties of natural organic acids (humic and fulvic acid), the overall acidity is factored into two where a lower pK_a value, normally around 4.2, represents the carboxylic distribution, while a higher pK_a value, normally around 9.1, represents the phenolic distribution [93WIT/RIE, 93WIT/RIE2]. This division yields an equivalent result as in the discrete approach by considering two major acidic sites.
- *The normal distribution model* [83PER/LYT, 87PER/PAR]. The Gaussian distribution model has been employed to distinguish a two ligand mixture from a continuous distribution of ligands [83PER/LYT].

Figure VI.6: Plot of $\text{p}K_a^{\text{app}}$ versus α (the degree of neutralization) for Laurentide fulvic acid as a function of ionic strength (note: data at $I = 1$ and 5 M are exactly superimposable).



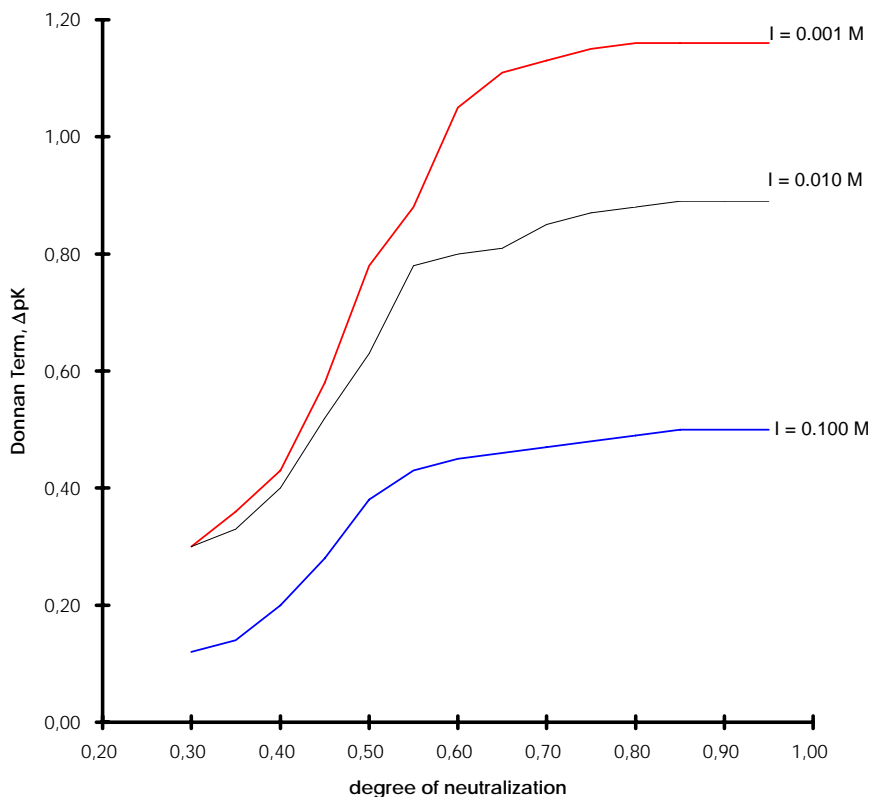
- *The differential equilibrium function model.* A continuous distribution of sites is assumed where the macroscopic binding functions are interpreted in terms of the microscopic binding constants [80GAM/UND, 88ALT/BUF, 88GAM/LAN].

VI.3.1.3. Discrete models versus continuous distribution models

The choice of which model to employ in the description of metal-humate interactions depends on the objective of the data analysis. The discrete ligand approach is easily adapted to experimental data using graphical methods [84FIT/STE] and as such amenable to the prediction of metal-humate interactions by incorporation into existing chemical speciation computer programs, *e.g.*, FITEQL [94HER/WES]. The disadvantages of the discrete ligand model are that the identified ligands may not be representative of the actual binding sites in the humic substance, the difficulty to extend it outside the range of calibration and the tendency to underestimate metal humate interactions at very low metal ion concentration [86DZO/FIS].

Whereas the continuous distribution models probably approach the complexity of nat-

Figure VI.7: Variation of the Donnan potential term, $\delta_p K$, with the degree of neutralization of Laurentide fulvic acid at three different ionic strengths. The curves have been obtained from the experimental data in Figure VI.6.



ural organic acids, their shortcoming is their inability to describe and predict the sequestering of metal ions. It has been argued that a continuous distribution model serves primarily as a first step towards identifying the most probable distribution of the acidic functionalities in natural organic acids [86DZO/FIS]. In effect, the application of the affinity distribution model [90WIT/RIE, 93WIT/RIE] is intrinsically similar to the discrete model when applied to humic substances [92BAR/CAB, 92TIP/HUR].

VI.3.2. Models for the interaction of metals with humic/fulvic acids

While both the discrete ligand and continuous distribution models recognise the heterogeneous multiligand nature of humic substances, their differences lie in the modelling of the substances and thus their approach of describing their interaction with metal ions [86DZO/FIS].

In situations where very little is known about the nature of humic substances, an “average” approach may be employed. An example of such an “average” approach is presented later in this chapter where the effect of humic substances on the speciation of

Table VI.1: Comparison of experimentally based overall degree of dissociation, $\alpha_{\text{exp}}^{\circ}$, of Laurentide fulvic acid in 1.00 M NaNO₃ with the summation of computed contributions of five different acid sites to overall degree of dissociation, $\alpha_{\text{calc}}^{\circ}$.

Acid Site Identity	$pK_{a,n}^{\text{int}}$	Acid Site Abundance, A_n	Acid Moiety
1	1.7	0.32	Carboxylic
2	3.0	0.21	Carboxylic
3	4.0	0.204	Carboxylic
4	5.1	0.14	Alcoholic OH
5	6.5	0.126	Alcoholic OH

$\alpha_{\text{calc}}^{\circ} = \sum \alpha_n A_n$							
pH	$\alpha_1 A_1$	$\alpha_2 A_2$	$\alpha_3 A_3$	$\alpha_4 A_4$	$\alpha_5 A_5$	$\alpha_{\text{calc}}^{\circ}$	$\alpha_{\text{exp}}^{\circ}$
3.434	0.314	0.154	0.044	0.003	0.000	0.514	0.511
3.516	0.315	0.161	0.050	0.004	0.000	0.530	0.526
3.607	0.316	0.168	0.059	0.004	0.000	0.548	0.549
3.725	0.317	0.177	0.071	0.006	0.000	0.570	0.570
3.869	0.318	0.185	0.087	0.008	0.000	0.598	0.598
3.953	0.318	0.189	0.097	0.009	0.000	0.613	0.616
4.178	0.319	0.197	0.123	0.015	0.001	0.654	0.657
4.324	0.319	0.201	0.138	0.020	0.001	0.679	0.681
4.725	0.320	0.206	0.172	0.042	0.002	0.741	0.744
5.014	0.320	0.208	0.186	0.063	0.004	0.781	0.783
5.359	0.320	0.209	0.195	0.090	0.009	0.823	0.827
5.833	0.320	0.210	0.201	0.118	0.022	0.871	0.874
6.453	0.320	0.210	0.203	0.134	0.060	0.927	0.924
6.794	0.320	0.210	0.204	0.137	0.084	0.954	0.949

Eu(III) in the environment is anticipated.

In both the discrete ligand and continuous distribution models, a mass-action parameter equivalent to the overall complex formation function, β_{ov} , is calculated as follows:

$$\beta_{\text{ov}} = \frac{\Sigma[\text{M}]_{b,i}}{[\text{M}^{z+}] \gamma_{\text{M}} \exp\left(\frac{-F\Psi}{RT}\right) \Sigma[\text{A}_i^-]} \quad (\text{VI.13})$$

where $\Sigma[\text{M}]_{b,i}$ is the sum of the concentrations of metal bound to all active sites; $[\text{M}^{z+}]$ is the free metal ion concentration; γ_{M} is the single ion activity coefficient of the metal ion under study; $\exp(-F\Psi/RT)$ is the electrostatic term [90WIT/RIE, 92BAR/CAB, 92TIP/HUR, 93WIT/RIE, 93WIT/RIE2] and $\Sigma[\text{A}_i^-]$ is the concentration of the dissociated portion of the fulvic acid molecule [91EPH/RED]. The model for the electrostatic term in the expression for β_{ov} for systems with metal ions has been recently questioned

[92BAR/CAB]. However, for systems with trace quantities of metal ions, *i.e.*, very high ligand to metal ion ration, the choice of the electrostatic term will introduce very small errors.

The overall complex formation function, β_{ov} , is not a thermodynamic quantity describing the various binding patterns to the various complexing sites. However, it can be used to compare, on a macroscopic level, results obtained from different experimental techniques [83TUS/BRE, 89EPH/XU]. Additionally, the overall complex formation function can be used in the three component system, metal ion – inorganic oxide – humic substances, to quantify the influence of humic substances on the adsorption of metal ions on such oxides [89XU/EPH].

VI.3.2.1. *Discrete ligand models*

This approach considers the humic substance as a heterogeneous multiligand, which could potentially bind metal ions both with and without the release of protons. The extent of proton release is a direct function of the pK_a of the acid and the free energy of complex formation, $\Delta_r G_m^\circ$. The overall equilibria may be described by considering each acid site to bind at most one metal-ion as follows:



This representation implies that at equilibrium, each active site, S_i , forms the “complex” $S_i M$. All these “species” are in equilibrium with each other and their relative concentrations are determined by their respective free energy of complexation, $\Delta_r G_m^\circ(S_i M)$. It is necessary to note that in this model, site-to-site interactions have not been incorporated, not because they do not exist, but rather because there is no method available for their determination. Combination of this bonding model with the acid-base properties as defined by the discrete ligand model [86EPH/MAR, 89EPH/MAR, 90TIP/RED, 92TIP/HUR, 92BAR/CAB] yields the following expression:

$$\left(\frac{\theta_M}{(1 - \theta_M)} \right) \frac{1}{[HA]_{TOT}} = \sum_{i=1}^n \left(\frac{\beta_i f_i}{1 + \frac{[H^+] \exp\left(\frac{-F\Psi}{RT}\right)}{K_i} + \beta_i [M^{z+}]_f \left(\exp\left(\frac{-F\Psi}{RT}\right)\right)^z} \right)$$

where θ_M is the fraction of metal bound, $[HA]_{TOT}$ is the total titratable acid in the system, β_i is the complex formation constant for reaction (VI.14), f_i is the fraction of the i^{th} site, K_i is the acid dissociation constant of the i^{th} site, and $\exp(-F\Psi/RT)$ is the electrostatic term which is obtained from potentiometric titrations of metal-free systems.

The binding of copper by a well characterised aquatic fulvic acid has been successfully described by this model [94EPH/ALL]. Furthermore, the various ways of bonding of Cu(II) in a soil fulvic acid have been suggested recently, following a modification of an earlier algorithm which takes the functional group heterogeneity existent in the fulvic acid [86EPH/MAR, 95MAR/RED] into account. In both cases mentioned above, stability

constants reported for the interaction between Cu(II) and the acid group postulated to be present in the fulvic acid have been employed.

The prediction of proton and metal ion binding to humic substances under different environmental conditions has also been made using with Tipping's model V [92TIP/HUR, 93TIP]. By using two types of acid groups, a good fit is obtained for the binding of copper by fulvic acid.

VI.3.2.2. Continuous distribution models

The Gaussian distribution model has been adapted to take competition between different metal ions into account (MINTEQA2) and employed to describe the binding of Al(III) and Cu(II) by humic substances [94ALL/PER]. An improvement in the model performance is obtained when both carboxylic and phenolic sites are incorporated into the calculations.

The affinity distribution model has also been extensively used to describe metal-humate interactions. A two pK_a model for the competitive binding of metal ions to humic substances [93WIT/RIE2] has been modified to a non-ideal competitive adsorption model (NICA) to describe the binding of H^+ , Cd(II), Cu(II), and Ca(II) to humic substances [95BEN/MIL]. To effect a satisfactory prediction of the experimental results, two classes of acidic functionalities are employed – the first with a median pK_a of 4.60, is assumed to be a carboxylic acid group, while the second with a median pK_a of 9.34, could refer to phenol, alcohol and enol- groups.

VI.3.2.3. Factors affecting the overall complex formation function

The overall complex formation function as expressed by Eq. (VI.13) assumes a 1:1 complex between the metal ion and the humic ligand. This assumption does not take the functional site heterogeneity of the humic substance molecule into consideration [93NOR/EPH, 94EPH/ALL]. The overall complex formation function is affected by ionic strength, pH, temperature, ratio of metal ion to humic substance and experimental method [78BRE/GRA, 79BER/KRA, 80LI/VIC, 83ALB/GIE, 83TUS/BRE, 85GAM/MAR, 87BUF/ALT, 88BUF, 89EPH/XU, 91EPH].

The effect of pH on the overall complex formation function for Eu(III) has been found to be method dependent [91EPH]. For example, while a pH dependence of the overall complex formation function was observed for the Eu(III)-fulvate system studied by the ion exchange distribution method, no such variation was observed using the ultrafiltration technique [91EPH, 93NOR/EPH, 94NOR]. Application of laser-induced fluorescence [91BID/GRE] and laser-induced photoacoustic spectroscopy [93KIM] gave a complex formation function which was not strongly dependent on pH in the range investigated. It must be pointed out that in both studies [91BID/GRE, 93KIM] buffers were employed while the other studies were made in the absence of buffers.

The effect of ionic strength on metal-humate interactions may be illustrated by the ratio of metal bound to free metal for the Eu(III)-fulvate system (Figure VI.8). A higher ratio of metal bound to free metal is obtained at a lower ionic strength (0.01 M $NaClO_4$) than at

the higher ionic strength (0.10 M NaClO₄). For the Eu–FA system, $\log_{10}([M]_b/[M^{z+}])_{0.01} - \log_{10}([M]_b/[M^{z+}])_{0.1}$ is $\approx 1.5 \log_{10}$ units using the ion exchange distribution technique, while the corresponding difference for the ultrafiltration method is $\approx 0.5 \log_{10}$ units. A theoretical value of $3 \log_{10}$ units difference is expected (as $\log_{10}(0.1/0.01)^3$). The fact that $\Delta \log_{10}([M]_b/[M^{z+}])_{I=0.01-0.1}$ is 1.5 instead of the theoretical value of 3 has been attributed to the small size of the fulvic acid molecule (as compared to typical synthetic polymers) and the functional group heterogeneity existent in the fulvic acid [86EPH/ALE]. However, the values indicate that the ion exchange distribution method yielded values much more sensitive to ionic strength effects, while the results of the ultrafiltration method were less sensitive to such effects [93NOR/EPH]. The discrepancy between these observations may be attributable to the differences in the experimental methods. In the ion exchange distribution method, the reactions involve an exchange of Eu(III) for Na⁺ in the resin. This reaction is strongly influenced by the ionic strength as shown by plots of $\log_{10} D_o$ versus $\log_{10} a_{\text{NaCl}}$. D_o is the distribution coefficient of Eu(III) in absence of fulvic acid, and a_{NaCl} is the activity of the bulk electrolyte [89EPH/MAR]. In the ultrafiltration method, filtration under pressure is effected under conditions where the bulk electrolyte has a retention coefficient of zero for the membrane. Hence, the effect of the ionic strength on the ratio of metal bound to free metal is expected to be minimal since the dependence of free metal determination on the bulk electrolyte concentrations is very small.

VI.3.2.4. Competitive binding of various metal ions to humic substances

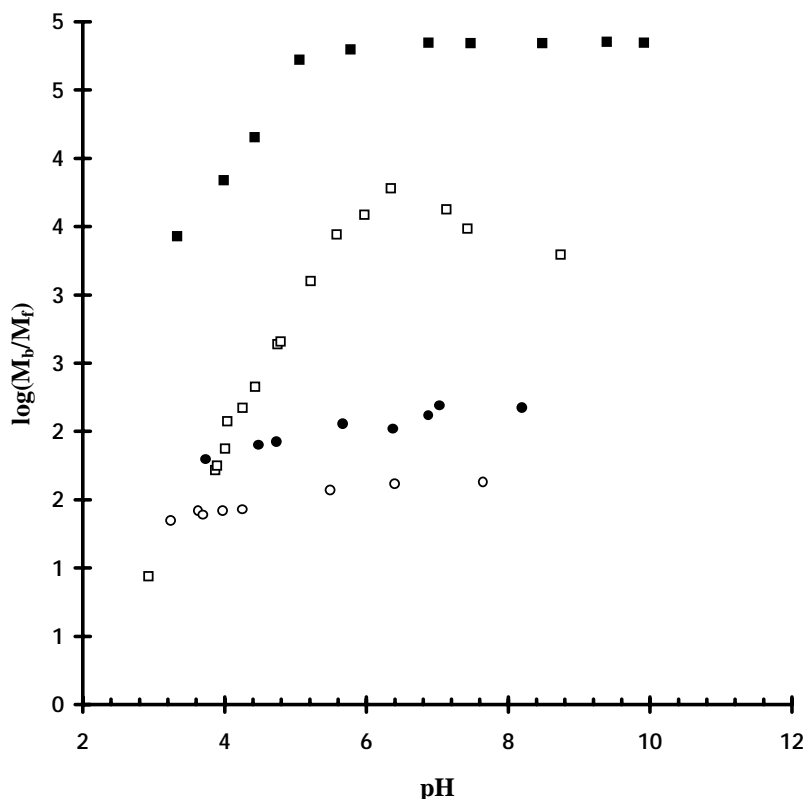
Different metals have different affinities for different ligands [81STU/MOR]. Metals have been classified using their affinity for the first ligand atom of each periodic group (*i.e.*, F, O, N) or with a later member of the group (*e.g.*, I, S, P), *cf.* Chapter III.

A-type metal cations have inert gas type (d^0) electron configuration and are normally visualised as hard spheres whose electron shells are not easily deformed. Examples of such metal cations are H⁺, Li⁺, Na⁺, K⁺, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Al³⁺, Sc³⁺, La³⁺, Si⁴⁺, Ti⁴⁺, Zr⁴⁺, and Th⁴⁺.

B-type metal cations are visualised as “soft spheres” with low electronegativity and high polarizability, *e.g.*, Cu⁺, Ag⁺, Au⁺, Tl⁺, Ga⁺, Zn²⁺, Cd²⁺, Pb²⁺, Sn⁺, Tl³⁺, Au³⁺, In³⁺, and Bi³⁺. While class A-type metal ions prefer ligands having oxygen as donor atoms and F, class B-type metal ions coordinate preferentially with bases containing I, S, or N as donor atom, *cf.* Section III.2.2.4 and Figure III.7 on *p.*86.

The competitive binding of various metal ions to humic substances must recognise the acceptor properties of the metal ion and the functional group heterogeneity in the humic substances [93TIP]. Various experimental evidence suggest that the humic substances have sufficient number of sites to bind different metals simultaneously. For example, in competitive binding studies involving Eu(III) and Sr(II), Eu(III) and Al(III) and Fe(II)/Fe(III) it has been observed that in all instances, the binding of Eu(III) by an aquatic fulvic acid was not significantly affected by Sr(II), Al(III) or Fe(II)/Fe(III) [94NOR]. Copper binding by fulvic acid has also been observed not to be affected by Ca²⁺ [88HER/MOR]. These observations seem to suggest that metal ions need not compete for the same sites

Figure VI.8: Ultrafiltration (UF) and ion-exchange distribution studies (IEDS) of the Eu(III)–FA system ($[FA] = 120 \text{ mg} \cdot \text{l}^{-1}$; $[Eu(III)] = 10^{-11} \text{ M}$). Variations of the fraction metal bound, M_b , to free metal, M_f , with changes in pH as a function of ionic strength. ■ IEDS, $I = 0.01 \text{ M NaClO}_4$; □ IEDS, $I = 0.10 \text{ M NaClO}_4$; ● UF, $I = 0.01 \text{ M NaClO}_4$; ○ UF, $I = 0.10 \text{ M NaClO}_4$.



in the fulvic/humic acid molecule as long as there are enough sites on the humic molecule compared to the total available metal ions.

VI.3.3. Data needs for modelling the role of humic substances

The need for accurate and reliable data in modelling cannot be overemphasised. Estimates of the concentrations of humic substances in soils, surface water and ground water are the first important data required to predict their role in the distribution of trace components [81THU/MAL, 82STE]. After determination of the total concentrations, *e.g.*, as milliequivalent carbon per liter, one must estimate the functional groups concentration. Typically, this is made by acid-base titrations of the humic substances [70GAM, 72GAM, 77ARA/KUM, 83DEM/OME, 86EPH/ALE, 93BON/FIS]. Since environmental conditions span a range of ionic strengths, it is always necessary to perform such titrations as a function of ionic strength and over a range of humic substance concentrations [86EPH/ALE, 89EPH/BOR]. Comparison of potentiometric titrations of surface

and groundwater fulvic acid samples show that the effect of ionic strength on the $\text{p}K_a^{\text{app}}$ versus α (degree of neutralization) curves differ for different fulvic acid samples [94NOR, 94PET/EPH]. Such effects generally depended on the molecular weight of the sample, but for samples with the same molecular weight the ionic strength effects were more pronounced the more polydisperse the sample [94NOR]. The lesson from these observations is that it is not appropriate to calculate electrostatic corrections based on molecular weight alone unless the dispersity in the molecules is included.

Potentiometric titrations of a number of fulvic acids isolated from different origins (12 samples) have been performed at different ionic strengths and compiled (Figure VI.9). The interesting feature of the Figure is the range of the variation of $\text{p}K_a^{\text{app}}$ versus α for all the fulvic acids at three ionic strengths (0.001, 0.010, 0.100 M NaClO_4). At each defined degree of neutralization, the difference between the highest and lowest $\text{p}K_a^{\text{app}}$ values is ≤ 2 , with the largest difference at lower degrees of dissociation (Figure VI.9). Such data indicate that despite the functional site heterogeneity in the humic substance molecules, some cautious generalizations may be made of their acid-base properties. For example, when modelling the role of humic substances on the distribution of metal ions in the environment, a first approximation could be made by selecting the $\text{p}K_a^{\text{app}}$ value at 50% dissociation to be $\sim 4.0 \pm 1.0$. Figure VI.9 may be considered as an attempt to determine the upper and lower boundaries of $\text{p}K_a^{\text{app}}$ versus α curves for humic substances under typical environmental conditions.

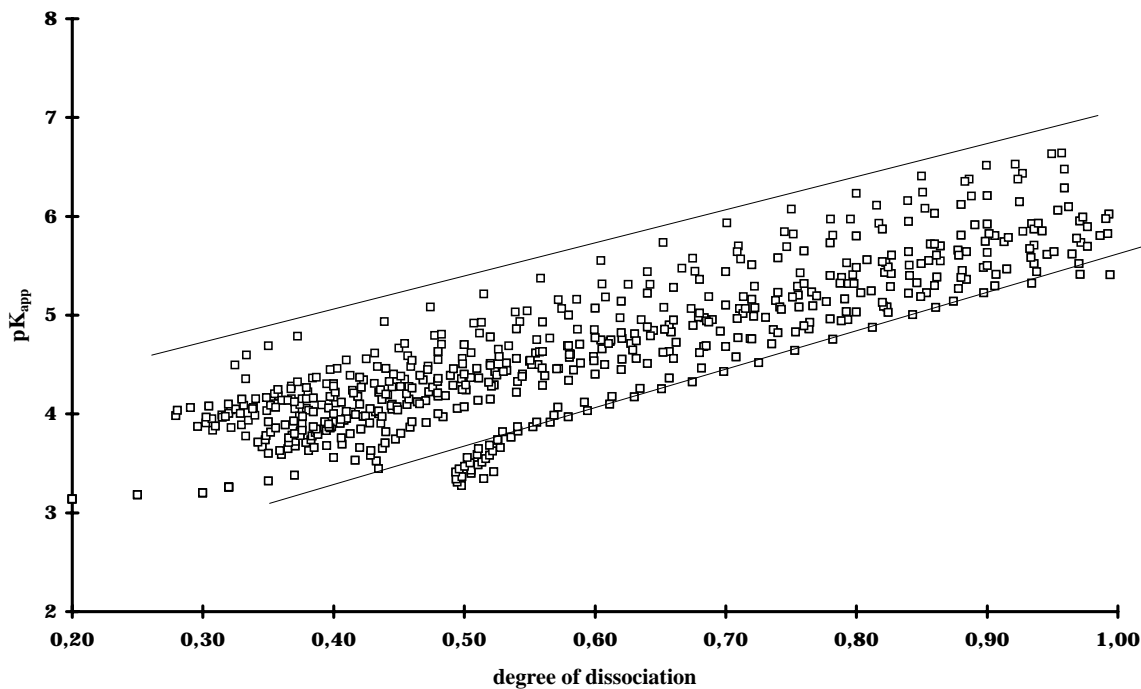
The active functional groups in humic substances may be identified and/or estimated using chemical derivatization techniques [92ARS/BOR] and spectroscopic methods, *e.g.*, FTIR, NMR [78RUG/SCI, 79RUG/INT, 80DER/MOR, 83GIL/WIL, 83HAT/BRE, 84PRE/SCH, 86GIL/WIL]. It is suggested that a combination of derivatization, spectroscopic and potentiometric titration techniques must be made to obtain a comprehensive picture of these substances [89EPH/BOR2].

The methods employed in metal binding studies are based on the determination of the concentrations of the components at equilibrium (free metal, free ligand or metal-ligand complex) without disturbing the equilibrium. Metal-humate studies ought to be conducted with concentrations of both ligand and metal ions which resemble those encountered in the environment. This requirement makes it impossible to use a number of experimental techniques. It has been suggested that metal-humate studies should be made using more than one experimental technique in order to identify the possibility of different reaction “windows” [83CAB/SHU, 83TUS/BRE, 89EPH/XU, 91EPH, 93NOR/EPH]. If two different experimental methods are used to study the same reaction, then the interaction parameters ($\log_{10} \beta_{\text{ov}}$) must be the same within the estimated uncertainty range [85FIS/MOR].

Studies of metal interaction with humic substances must be conducted at more than one ionic strength in order to describe how changes in bulk electrolyte concentrations which may occur in the environment (*e.g.*, saline waters in marine environments) influence the metal-binding [94EPH/ALL].

There is a need to compile potentiometric titration and metal-humate binding data to facilitate the meaningful generalizations which are necessary when modelling metal-ion

Figure VI.9: Acid-base titration curves (pK_a^{app} versus α) for 12 different aquatic fulvic acid samples at different ionic strengths (0.10, 0.01 and 0.001 M NaClO_4). Visualise the curve as providing the upper and lower boundaries for the titration curves for the 12 fulvic acid samples [95EPH/PET].



interactions with organics in the environment.

Efforts to incorporate humic and fulvic acid complexation into existing chemical equilibrium models or speciation codes must begin with the definition of their concentration. In absence of an easily determined molecular weight, concentration determinations have been made using either equivalent per litre ($\text{eq} \cdot \text{l}^{-1}$) or gram per litre ($\text{g} \cdot \text{l}^{-1}$) [91MOU/CAC]. Since most equilibrium constants employed in the speciation codes (FITEQL, PHREQEE) are expressed as $\text{l} \cdot \text{mol}^{-1}$, it would be more convenient to express the parameter describing metal-humate interactions in similar units. Such an option will thus demand that the acid capacities of a large number of humic and fulvic acids be determined (equivalents per gram of humic material) to facilitate the choice of a representative mean value (a function of the origin of the humic substances) [82STE, 94PET/EPH] which can be used to convert the unit $\text{g} \cdot \text{l}^{-1}$ into $\text{eq} \cdot \text{l}^{-1}$. Since protons are the basis for the potentiometric titration measurements, the $\text{eq} \cdot \text{l}^{-1}$ units are the same as the molar units which are usually employed in speciation computer programs. An example of initial estimates that may be made to anticipate the effects of humic/fulvic acids on the speciation of trace metals in the environment is presented in Section VI.4.

VI.3.3.1. Review of studies on interactions between humic substances and metal ions

Metal-humate interactions have been studied for a long time employing various experimental methods. A brief presentation of some of them are given in this Section.

VI.3.3.1.1. Anodic stripping voltammetry

This method which has been used for studying the interaction between humic substances and metals ions (Cd^{2+} , Cu^{2+} and Zn^{2+}) utilises the possibility to determine the free metal ion in the presence of the humic substance [73SHU/WOO, 87BUF/VUI]. The method is based on the fact that the rate of reduction of the free metal ion is very rapid, while the rate of dissociation of the metal-humate complex is much slower. The possible dissociation of the metal-humate complex and/or the humic material is a major disadvantage of this method.

VI.3.3.1.2. Fluorescence spectroscopy

Even though only a small fraction of humic substances exhibit fluorescent properties, the method is employed for studies of metal-humate interactions especially involving paramagnetic transition metal ions such as Cu^{2+} , Fe^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cr^{3+} [80SAA/WEB, 83RYA/HOL, 90SEN]. Additionally, the fluorescent properties of selected metal ions, *e.g.*, Eu^{3+} , have been utilised in Eu(III)-fulvate system [91BID/GRE].

VI.3.3.1.3. Equilibrium dialysis

The utilisation of membranes of varying sizes to separate free metal ions from the ligand and complex has found considerable use. The drawback of the method is the possible sorption of species onto the surface of the dialysis membrane [81TRU/WEB, 82RAI/WEB, 85CAR].

VI.3.3.1.4. Ion-selective electrodes

The availability of specific electrodes for a number of metal ions has allowed the in situ determination of free metal ion concentrations in metal-humate mixtures. The metal ions for which ion-selective electrodes have been developed include Cu^{2+} , Pb^{2+} , Ca^{2+} and Cd^{2+} [77BUF/GRE, 77STE, 78BRE/GRA, 80GAM/UND, 80SAA/WEB, 83TAK/YOS, 86EPH/MAR, 86FIT/STE, 86TUR/VAR, 87TUR/VAR, 89EPH/XU, 94EPH/ALL]. Recent developments of electrodes for lanthanides and actinides have met with serious drawbacks because of the narrow pH range in which they show Nernstian behaviour. Another disadvantage of these electrodes is the possible poisoning of the electrodes by humic substance coatings of the electroactive membrane of the electrode, leading to serious errors [85FIS/MOR].

VI.3.3.1.5. Ultrafiltration

The separation of species on the basis of their size is employed in the ultrafiltration method where the fulvic acid molecule and the complex are separated from the free metal ion [76SMI, 83STA/BUF, 84BUF/STA, 84STA/BUF, 90EPH/MAR, 91EPH]. Precautions needed for the method include avoiding low-molecular weight fragments filtering through the membrane, and possible dissociation of the metal-humate complex.

VI.3.3.1.6. Gel filtration chromatography

A method generally employed for size evaluation is adapted for metal-humate studies [75MAN/RIL, 77MEA/CRE, 81HIR]. The metal ion concentrations associated with the separated sizes (fractions) are determined, thus allowing a determination of the fractions mostly involved in the binding. Cu^{2+} , Zn^{2+} , Mn^{2+} and their interactions with humic acids have been studied using this method.

VI.3.3.1.7. Solvent extraction

The effect of humic substances on the partition of metal ions in an aqueous and non-aqueous medium is employed to determine formation functions for metal-humate complexes [83TOR, 84TOR/CHO]. Metal ions may be employed both at macro or micro-concentration levels, *i.e.*, 10^{-2} to 10^{-5} M, or 10^{-6} to 10^{-11} M for radioisotopes, *e.g.*, ^{152}Eu , ^{109}Cd , ^{65}Zn , *etc.*

VI.3.3.1.8. Ion exchange distribution

An indirect approach is employed to estimate the ratio of metal bound to free metal [48SCH]. Such an approach has found a useful application in studies involving humic substances and metal ions like Co^{2+} , Zn^{2+} , Eu^{3+} , Cd^{2+} [67SCH/SKI, 72ARD/STE, 72ZUN/GAL, 89EPH/MAR, 91EPH, 93NOR/EPH].

VI.4. Modelling example: speciation of Eu^{3+} in the environment in presence of humic substances and Ca^{2+}

It must be noted that “real” systems do contain other substances in addition to humic substances, *e.g.*, inorganic colloids and particulates, low molecular weight organic and inorganic substances, microorganisms such as fungi and bacteria, *etc.* Since all the models discussed in this chapter are based on laboratory data from binary systems, their application to “real” systems may be questioned. In the models discussed, the interaction between metal ion, humic substances and geologic solids such as FeOOH , alumina, *etc.* has not been considered, and such ternary equilibria are known to influence the distribution and mobility of trace metal ions in the environment. The question then is –

what are the benefits of these models? The clear advantage of the models is that they use accepted “knowledge”, *e.g.*, Debye-Hückel, Boltzman Distribution, Gibbs-Duhem free energy considerations, to describe the solution chemistry of humic substances. In all the models, the important objective has been to adapt these to the humic substance systems and verify how well they may be described and/or predicted. The models provide the “basic knowledge” needed to facilitate the description of real systems.

In the light of the above discussion, our example of the possible effect of humic substances on the distribution and mobility of Eu^{3+} has used an “average” approach. The assumptions and parameters estimates employed are listed below and in Table VI.2.

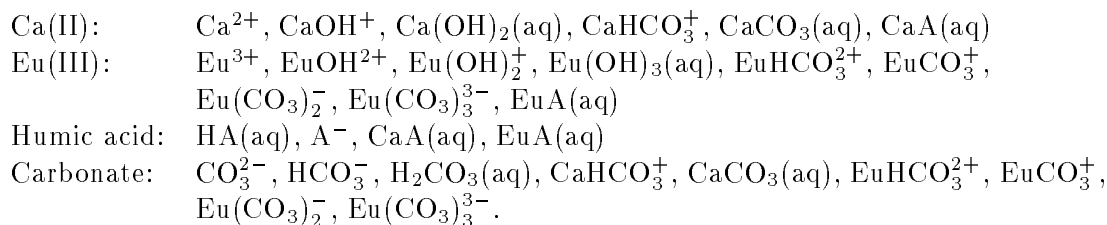
- a) the average acid capacity for humic substances (14 FA samples) = $5.1 \text{ meq} \cdot \text{g}^{-1}$
- b) average $\text{p}K_a^{\alpha=0.5}$ (from composite Figure VI.9) = 4.0
- c) $p\text{CO}_2 = 10^{-3.5} \text{ bar}$.

Depending on the concentrations of the humic substances, three scenarios have been used. In the first, all dissolved organic acid, DOC, in surface water is assumed to be humic substances. This assumption, gives the highest concentration of humic substances. The second scenario designates all the DOC in ground water as humic substances while the third option considers 15% of the DOC in groundwater systems ($1 \text{ mg} \cdot \text{l}^{-1}$) as humic substances.

The concentration in $\text{meq} \cdot \text{l}^{-1}$ is obtained from the concentration in $\text{mg} \cdot \text{l}^{-1}$ multiplied by the average acid capacity of $5.1 \text{ meq} \cdot \text{g}^{-1}$.

Typical concentrations of dissolved organic carbon in (surface) waters is less than or equal to $2 \text{ mg} \cdot \text{l}^{-1}$, while those for groundwater are less than $1 \text{ mg} \cdot \text{l}^{-1}$ [81THU/MAL]. In surface water systems 50% of the DOC is considered to be humic substances, while in the groundwater environments only 15% is humic substances, as determined by their adsorption characteristics on XAD-8 resins. The average concentrations of Ca^{2+} determined in ground and surface water are $10^{-2.9}$ and $10^{-3.8}$ [81STU/MOR, p.551]. The objective of the exercise is to estimate the role of organic acids in the speciation of the trivalent metal ion, *e.g.*, Eu(III) with a concentration of 10^{-8} M in an aquatic system.

The following 20 species, excluding solids, biota and colloids, have been considered in the model calculations:



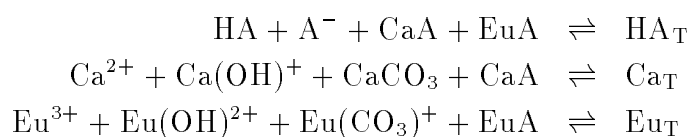
To simplify the situation, only the first hydroxide complexes and the carbonate complexes are considered for Ca(II) and Eu(III) . In both surface and ground water environments, it has been assumed that the system may be considered similar to an aqueous

carbonate system open to the atmosphere with constant CO₂(g) pressure. As a result the CO₃²⁻ concentration may be calculated at each pH using the relationship:

$$[\text{CO}_3^{2-}] = K_1 K_2 K_H \frac{p_{\text{CO}_2}}{[\text{H}^+]^2}$$

where K_1 , and K_2 are the first and second dissociation constants of the acid H₂CO₃(aq), K_H is Henry's Law constant and p_{CO_2} is the pressure of CO₂ [81STU/MOR, p.179–182]. The various values employed in this example are: $K_1 = 10^{-6.3}$, $K_2 = 10^{-10.23}$, $K_H = 10^{-1.5}$ and $p_{\text{CO}_2} = 10^{-3.5}$ bar.

The concentrations of the different species were calculated using the material balance for the various components, *i.e.*, Ca(II), Eu(III), humic acid and carbonate, and the charge balance. The material balance considerations for the three major substances, humic substance, HA, calcium, and europium are given in the following equations:



For Ca²⁺ and Eu³⁺, the following general expression may be used, provided only binary complexes are formed:

$$M^{z+} = M_{\text{total}}^{z+} / (1 + \sum \beta_j L_j)$$

where j is the complex and L_j is the ligand of the complex, M^{z+} is the free metal concentration at equilibrium, M_{total}^{z+} is the total amount of metal initially added or present and β_j is the stability constant of the complex.

For the humic material (in this particular example), the following expression holds, provided only binary complexes are formed:

$$\text{A}^- = \text{HA}_T / (1 + h / K_a^{\text{diss}} + (\beta_{\text{CaA}} \text{Ca}^{2+}) + (\beta_{\text{EuA}} \text{Eu}^{3+}))$$

where HA_T is the total concentration of humic substances, A⁻ is the concentration of the anion of humic substance, h is the proton concentration, K_a^{diss} is the overall dissociation constant for the humic substance, β_{CaA} is the constant for the calcium complexation by the humic substance, Ca²⁺ is the concentration of calcium ion, β_{EuA} is the constant for the complexation between europium and the humic substance and Eu³⁺ is the concentration of europium ion.

First an overall pK_a of 4.0 was selected to be representative of the humic substance. The choice of this value was based on the plot of pK_a^{app} versus α for a number of aquatic and terrestrial humic substances (Figure VI.9). In addition, it was assumed that Ca²⁺ and Eu³⁺ did not interfere with one another on binding to the organic acid. This assumption is based on results from our laboratory where the interaction of Eu(III) and an aquatic fulvic acid was not influenced by strontium, aluminium or iron [94NOR]. Similar lack

Table VI.2: Concentrations and equilibrium constants used in the calculation of the speciation of $\text{Eu}(\text{III})$ in ground and surface waters.

	Surface water	Groundwater	Low conc. of humic substances
[HA]	$2 \text{ mg} \cdot \text{l}^{-1}$	$1 \text{ mg} \cdot \text{l}^{-1}$	$0.15 \text{ mg} \cdot \text{l}^{-1}$
[Eu]	$1.0 \times 10^{-8} \text{ M}$	$1.0 \times 10^{-8} \text{ M}$	$1.0 \times 10^{-8} \text{ M}$
[Ca]	$1.58 \times 10^{-4} \text{ M}$	$1.26 \times 10^{-3} \text{ M}$	$1.58 \times 10^{-4} \text{ M}$

Stability constants:

Species	$\log_{10} \beta$	Reference
CaOH^+	1.3	[83HOG]
$\text{CaCO}_3(\text{aq})$	3.1	[81STU/MOR]
CaA	3.07	[93MAT/EPH]
EuOH^{2+}	6.32	[93KIM]
EuCO_3^+	5.93	[83HOG]
$\text{EuA} (1)$	5.1	[91EPH, 93NOR/EPH]
$\text{EuA} (2)$	$3.84 + 0.74(\text{pH})$	[93NOR/EPH]
$\text{EuA} (3)$	6.5	[93KIM]

of interference has been observed for the interaction of Cu^{2+} and fulvic acid upon the addition of Ca^{2+} [88HER/MOR]. The concentrations under different conditions and the stability constants employed for the various complexes are summarised in Table VI.2.

The calculated percentages of the various species as a function of pH are shown in Figures VI.10, VI.11, VI.12. The various cases studied indicate that the sequestering of $\text{Eu}(\text{III})$ in the presence of $\text{Ca}(\text{II})$ depends strongly on the value of the equilibrium constant describing the interaction between Eu and HA . A pH-independent $\log_{10} \beta_{\text{EuA}}$ value of 5.10 [93NOR/EPH, 91EPH] gave, for a surface water system where the HA concentration is $2 \text{ mg} \cdot \text{l}^{-1}$, that more than 50% of the $\text{Eu}(\text{III})$ was sequestered by the HA in the pH range of 5 to 7 (Figure VI.10). However, at $\text{pH} \geq 8$, the EuCO_3^+ complex becomes the predominant species. An equilibrium constant of $\log_{10} \beta_{\text{CaA}} = 3.07$ was chosen for the interaction between $\text{Ca}(\text{II})$ and humic substance [93MAT/EPH]. The speciation diagram shows that the binding of $\text{Ca}(\text{II})$ by humic substances is weak and that $\text{CaCO}_3(\text{aq})$ becomes the predominant $\text{Ca}(\text{II})$ species after pH of 9.0. At $\text{pH} \leq 9$, Ca^{2+} remains the predominant species.

Figure VI.10: Speciation of Eu(III) in a typical surface water environment. $[HA] = 1.0 \times 10^{-5} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = 5.1$.

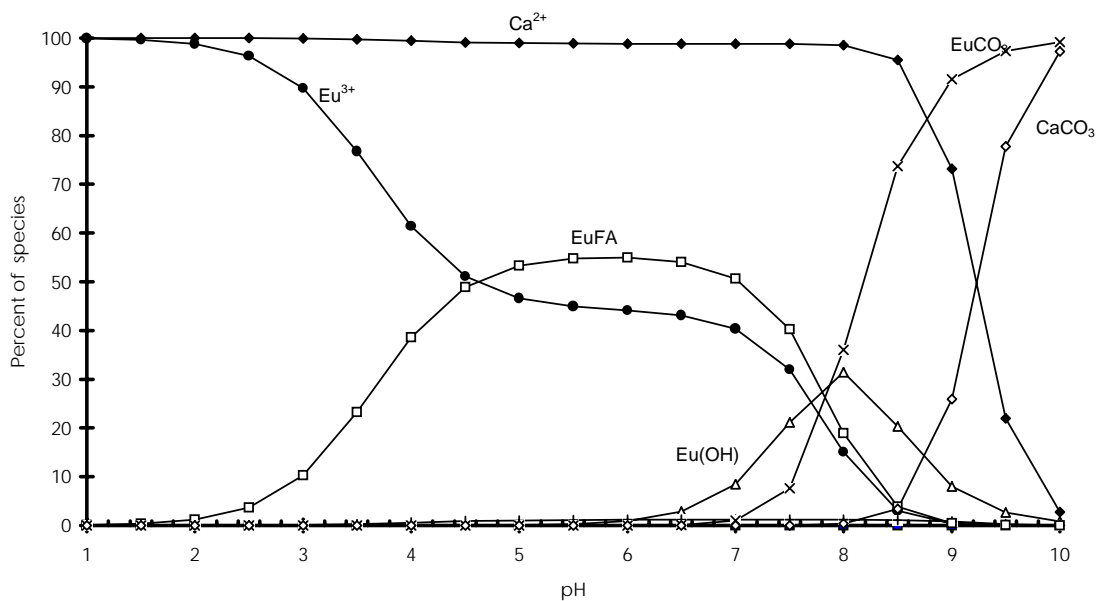


Figure VI.11: Speciation of Eu(III) in a typical surface water environment. $[HA] = 1.0 \times 10^{-5} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = (3.04 + 0.74(\text{pH}))$.

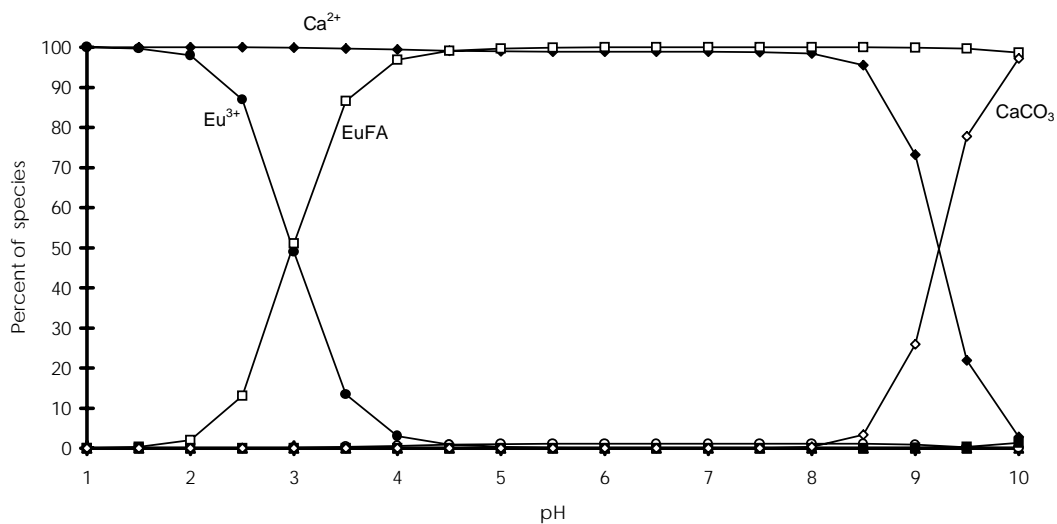
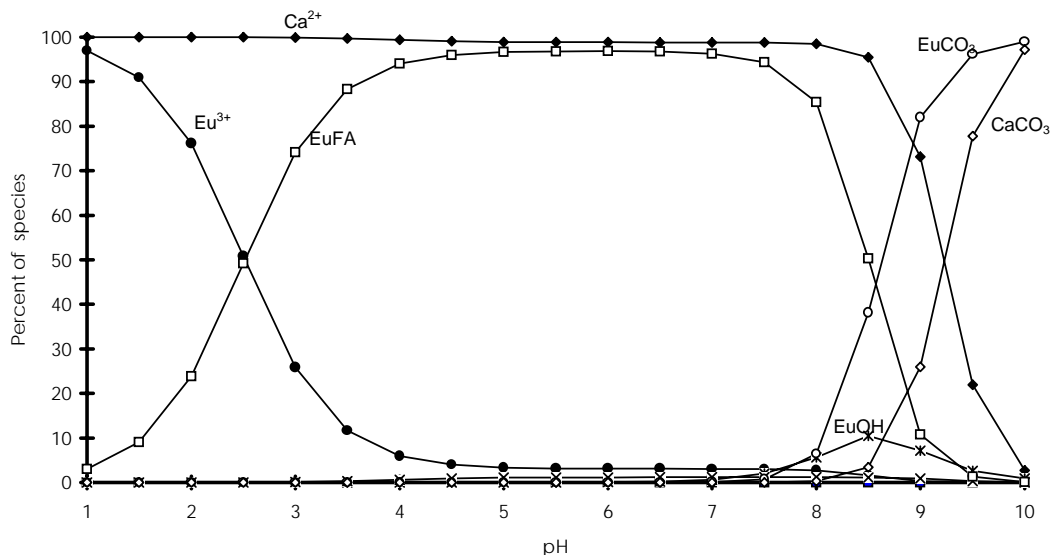


Figure VI.12: Speciation of Eu(III) in a typical surface water environment. $[\text{HA}] = 1.0 \times 10^{-5} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = 6.5$.



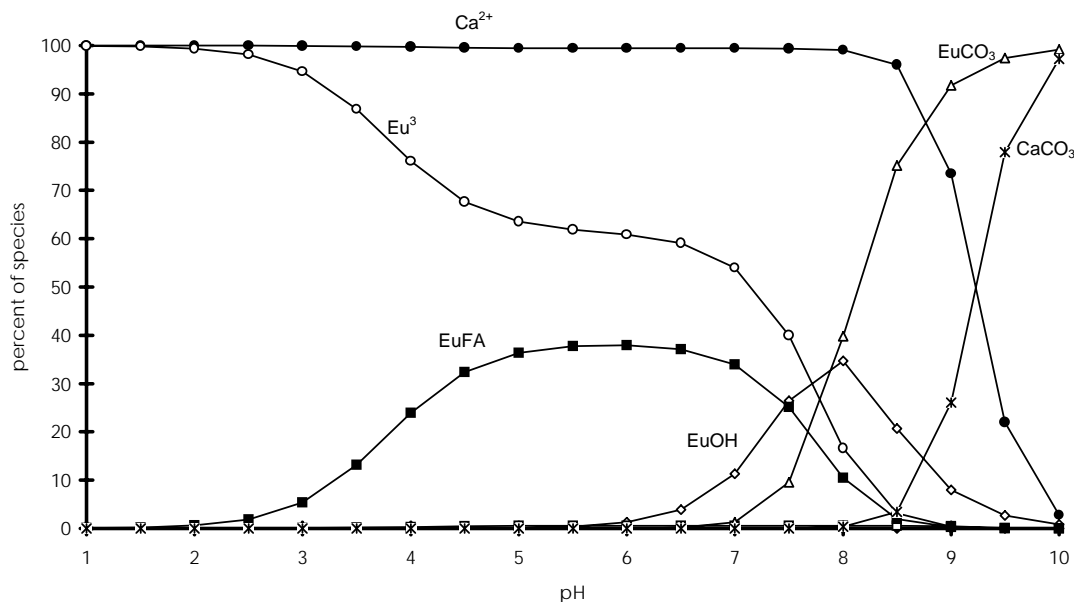
Using a pH dependent value of $\log_{10} \beta_{\text{EuA}}$ obtained from ion exchange distribution studies, [93NOR/EPH] gives a completely different picture (*cf.* Figure VI.11). In this case, the Eu(III) is completely bound by the humic substance at pH values ≥ 4.5 , and EuCO_3^+ is not formed in appreciable amounts. The speciation with respect to Ca(II) is not affected by the change in $\log_{10} \beta_{\text{EuA}}$ because of the assumption of non-interference.

The choice of $\log_{10} \beta_{\text{EuA}}$ is difficult since the literature is swamped with a multitude of different values. A compromise pH-independent value of 6.5 (*cf.* Table VI.2) has been chosen for $\log_{10} \beta_{\text{EuA}}$ [93KIM] and employed in the calculations shown in Figure VI.12. With this value, the $\text{EuA}(\text{aq})$ complex predominates at pH values ≤ 8.5 and the $\text{EuCO}_3(\text{aq})$ complex at pH > 8.5 . The EuOH^{2+} complex reaches a maximum (10%) at pH 8.5 and drops again as the pH increases (Figure VI.12).

In most groundwater systems, the amount of DOC is about 50% of the surface water DOC value, *i.e.*, $1 \text{ mg} \cdot \text{l}^{-1}$. By assuming that the binding characteristics of the DOC are dominated by the characteristics of the humic substances, that the ground water is open to $\text{CO}_2(\text{g})$ at a constant atmospheric pressure as in the surface water system and by employing a pH-independent $\log_{10} \beta_{\text{EuA}}$ of 5.10, we find the results shown in Figure VI.13. At pH values < 7.5 , Eu^{3+} ions predominate. The $\text{EuA}(\text{aq})$ complex formed reaches a maximum of 40% at pH of 5.0, remaining at the same level until pH of 7 and then drops down (Figure VI.13). At pH ≥ 8.0 , the $\text{EuCO}_3(\text{aq})$ complex becomes the predominant species.

Application of the pH-dependent function for the $\log_{10} \beta_{\text{EuA}}$ shows that the $\text{EuA}(\text{aq})$ complex takes over as the predominant species at pH values ≥ 3.5 where all Eu(III) is

Figure VI.13: Speciation of Eu(III) in a typical groundwater environment. $[HA] = 5 \times 10^{-6} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = 5.1$.



essentially sequestered by the humic substance (Figure VI.14).

When a $\log_{10} \beta_{\text{EuA}}$ of 6.5 is employed in the exercise, it is observed that the $\text{EuA}(\text{aq})$ complex predominates in the pH range of 3 to 8. However, at pH values > 8 , the $\text{EuCO}_3(\text{aq})$ complex becomes the predominant species (Figure VI.15).

Finally, the situation in which the humic substance will have the smallest effect on the Eu(III) speciation will be considered. This situation will be a typical groundwater environment where not all the $1 \text{ mg} \cdot \text{l}^{-1}$ DOC belong to humic substances but only 15% of the DOC are humic/fulvic acids (*cf.* Section VI.2). The concentration of humic substances thus will be $7.5 \times 10^{-7} \text{ eq} \cdot \text{l}^{-1}$. Employing the lowest $\log_{10} \beta_{\text{EuA}}$ value of 5.10 yields the speciation diagram shown in Figure VI.16. In this figure, it is shown that the $\text{EuA}(\text{aq})$ complex constitutes less than 10% of the Eu(III) species in the pH range of 4 to 8. The EuOH^+ complex reaches a maximum (40%) at pH of 8 where the carbonate complex, EuCO_3^+ becomes the predominant species. This picture is however, considerably changed when a $\log_{10} \beta_{\text{EuA}}$ value of 6.5 is employed (Figure VI.17). With this value, the $\text{EuA}(\text{aq})$ complex becomes the predominant species in the pH range of 4 to 7.5. The carbonate complex again becomes the predominant species at pH values > 8 . Application of the $\log_{10} \beta_{\text{EuA}}$ as a function of pH even with such low concentrations of HA will indicate that the $\text{EuA}(\text{aq})$ complex becomes the predominant species of the Eu(III) speciation (Figure VI.18).

Modelling example: speciation of Eu^{3+}

Figure VI.14: Speciation of $\text{Eu}(\text{III})$ in a typical groundwater environment. $[\text{HA}] = 5 \times 10^{-6} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = (3.8 + 0.74(\text{pH}))$.

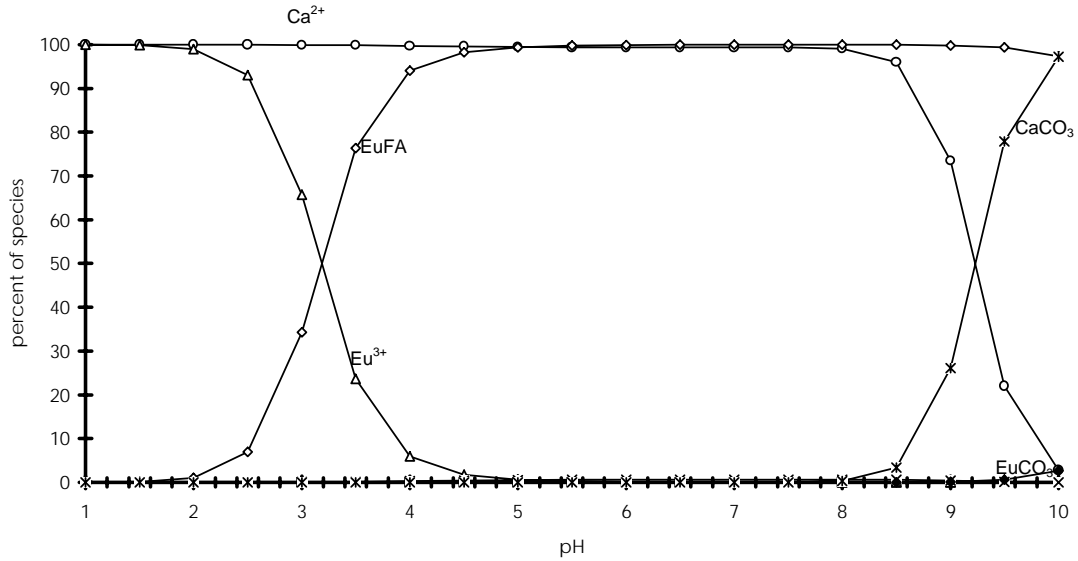


Figure VI.15: Speciation of $\text{Eu}(\text{III})$ in a typical groundwater environment. $[\text{HA}] = 5 \times 10^{-6} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = 6.5$.

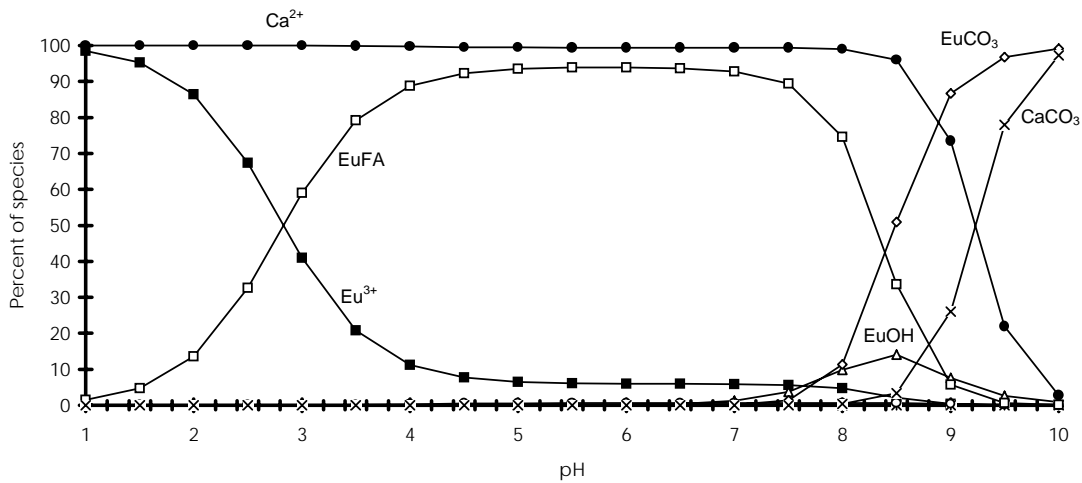


Figure VI.16: Speciation of Eu(III) in an environment with the lowest possible concentration of humic substances. $[HA] = 7.5 \times 10^{-7} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = 5.1$.

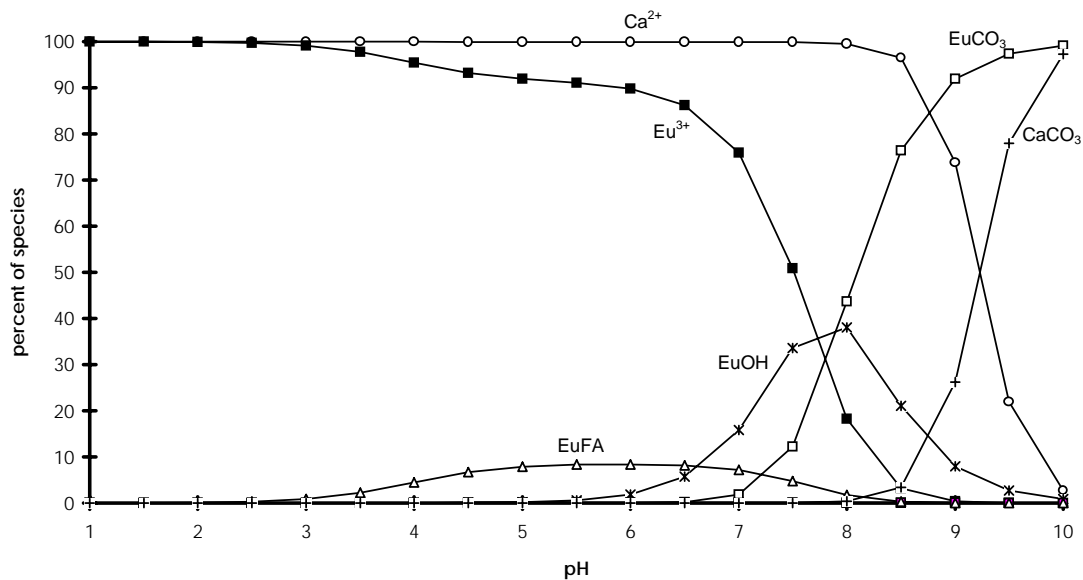
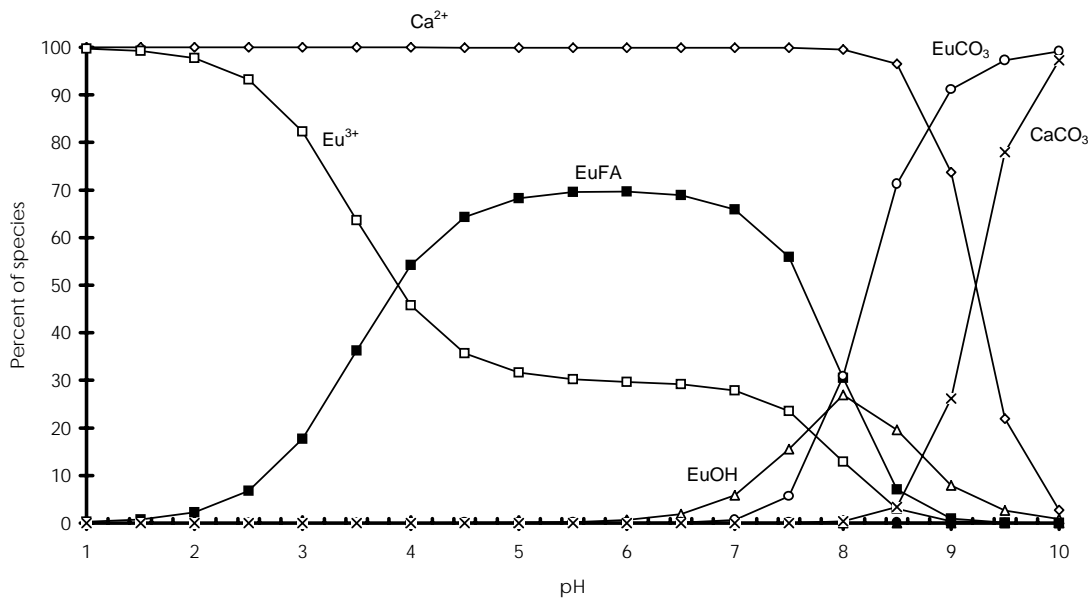
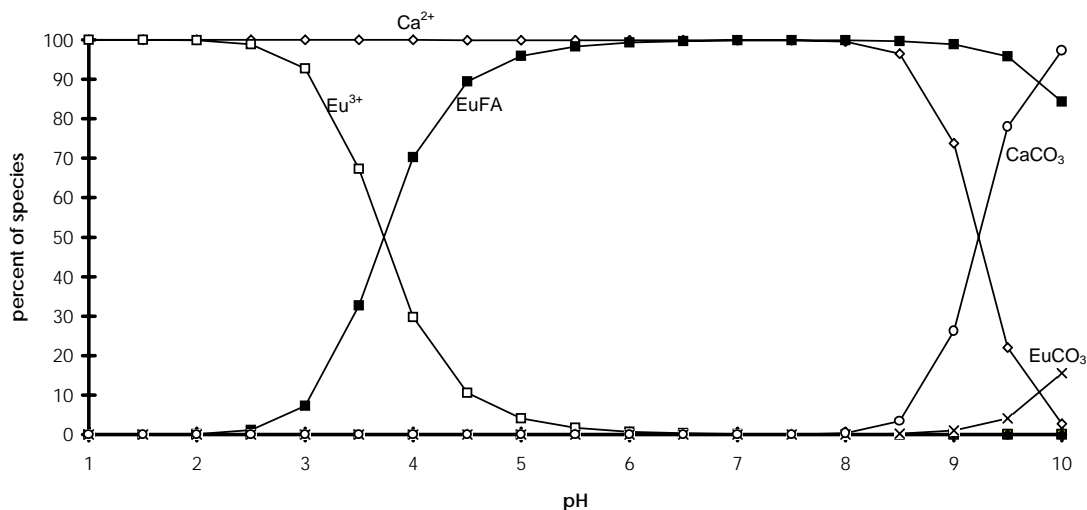


Figure VI.17: Speciation of Eu(III) in an environment with the lowest possible concentration of humic substances. $[HA] = 7.5 \times 10^{-7} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = 6.5$.



Summary

Figure VI.18: Speciation of Eu(III) in an environment with the lowest possible concentration of humic substances. $[HA] = 7.5 \times 10^{-7} \text{ eq} \cdot \text{l}^{-1}$, $\log_{10} \beta(\text{EuA}) = (3.84 + 0.74(\text{pH}))$.



VI.4.1. Relevance of the exercise

This example shows that both in groundwater and surface water environments, the speciation of trace toxic elements may be affected by the organic carbon component. The magnitude of this effect which is directly dependent on the concentrations of the organic matter, will be significant under acidic conditions. Under basic conditions, the carbonate complex (*e.g.*, EuCO_3^+) seems to predominate, especially for groundwater systems where the concentrations of DOC are small ($< 1 \text{ mg} \cdot \text{l}^{-1}$). Addition of the second carbonate and hydrolysis complexes for Eu does not change the picture, *i.e.*, influence of humic substances on the speciation of Eu in the environment. It must, however, be pointed out that the above exercise has been performed without the inclusion of organic acids which are associated with particles and colloids. To obtain a complete picture, one needs to incorporate the interaction of these organic components with inorganic colloids and particulates and microbial species [89XU/EPH, 94KRA/ALL, 94NOR/EPH]. However, it is unlikely that such a model will be particularly helpful for the modelling of “real” systems.

VI.5. Summary

The interaction of metal ions with natural organic acids has been examined by the representation of humic substances as typical natural organic acids. The possible formation pathways of these organic acids especially in aquatic environments has been briefly mentioned and the resultant functionalities which are responsible for their high affinity for metal ions have been considered. The concentrations of these natural organic acids in

the aquatic environments and the isolation and characterisation techniques have been discussed. The lack of information on molecular structure, weight, and configuration has resulted in different model structures for the description of the solution chemical properties of these systems. Two models predominate: the discrete multiligand model and the continuous distribution model. Current advances have shown that the two models actually converge with respect to the functional group heterogeneity in these substances. It was shown with an example that natural organic acids will have significant effect on the distribution of a trace element especially in surface water systems under acidic conditions. Such an effect is dependent on the concentrations of the organic acids, the model employed to estimate the extent of interaction between the metal ion and natural organic acid and the pH of the bulk solution. In groundwater systems open to the atmosphere, the role of humic substances in the speciation of toxic elements is partially reduced due to their small concentrations. The parameters necessary to describe/model the binding of metal ions by humic substances are described in Table VI.3.

Summary

Table VI.3: Parameters used in describing/modelling metal ion binding by humic substances.

Parameters	Comments	References
1. Concentration of organic matter in terrestrial and aquatic environments.	In terrestrial environments, units are $\text{g} \cdot \text{C} \cdot \text{g}^{-1}$ soil; in aquatic environment, units are $\text{g} \cdot \text{C} \cdot \text{l}^{-1}$.	[72SCH/KHA], [82STE], [91MAL]
2. Fraction of humic substance in organic matter		
3. Molecular weight of humic material	range from less than 700 to over 200 000 for humic and fulvic acids; humic acids have higher molecular weight than fulvic acid.	[69HAN/SCH], [85AIK/MCK], [89HAY/MCC]
4. Elemental analysis	Major elemental composition - C (55-44%); H (5-3%); O (37-52%); N (~1%); P (< 1%); S (~1%); Cl (< 1%)	[82STE], [85AIK/MCK], [89HAY/MCC]
5. Acid-base characteristics		
Acid capacity	range from 1 to 10 $\text{meq} \cdot \text{g}^{-1}$; fulvic acids generally have higher acid capacity than fulvic acid.	[72GAM], [72SCH/KHA], [82STE], [85AIK/MCK], [86EPH/ALE]
Radius of humic substance molecule	a rigid sphere is normally assumed.	[92BAR/CAB], [92TIP/HUR], [93WIT/RIE]
$\text{p}K_{\text{app}}$ vs. α curve	provides insight into both molecular weight heterogeneity and functional group.	[86EPH/ALE], [89EPH/BOR], [95EPH/PET]
Electrostatic effects	corrects deviation from ideality as a result of group-group interaction accompanying ionization process.	[84MAR/RED], [85GAM/MAR], [86DZO/FIS], [86EPH/ALE], [92BAR/CAB], [92TIP/HUR], [93WIT/RIE]

Table VI.3 (continued)

pK_{intr}	assumed overall intrinsic pK ; does not represent the true nature of humic substances but only used as a crude estimation. Normally, two values are assumed - one for -COOH and the other for -OH.	[84MAR/RED], [84MAR/RED2], [83PLE/JOS]
6. Functional groups		
Functional group heterogeneity	reactivity of humic substances is attributed to the high presence of oxygen-containing functional groups, <i>e.g.</i> -COOH, -OH <i>etc.</i>	[82STE], [85AIK/MCK]
Percentage of predominant acid sites	normally obtained by potentiometric titrations, pyrolysis, derivatization techniques, NMR <i>etc.</i>	[86EPH/ALE], [89EPH/BOR], [89EPH/BOR2], [92ARS/BOR]
pK_a of the sites	these values are normally guesses employed to fit experimental data.	[85PAX/WED], [86EPH/ALE], [92TIP/HUR], [92BAR/CAB]
7. Concentration of total metal ion		
values employed in modelling exercise should be close to environmental values.		
8. Concentration of free metal ion		
	methods employed include anodic stripping voltametry, fluorescence spectroscopy, equilibrium dialysis, ion-selective electrode, ultrafiltration, gel filtration chromatography, solvent extraction, ion exchange distribution.	[72ARD/STE], [75MAN/RIL], [78BRE/GRA], [82STE], [83RYA/HOL], [83TOR], [84TOR/CHO], [89EPH/MAR], [93NOR/EPH]
9. Stability constants of the metal-humate complex		
	explicit definition of the constants employed is mandated; comparison of values obtained for same metal-humate system using different methods.	[72ARD/STE], [73SHU/WOO], [81HIR], [83TAK/YOS], [94EPH/ALL]