Part 2. The Hydrosphere

Chapter 13. Metals in Water

Chapter 13. Metals in the hydrosphere 13.1 Aquo complexes of metals

 Aquo complex: exists where no other ligand is available to form complexes with a metal in aq. solution.

 $\rm M(H_2O)_a{}^{b+} + H_2O \rightarrow \rm M(H_2O)_{a-1}(OH)^{(b-1)+} + H_3O^+$, or simply

 $\mathsf{M}^{\mathsf{b}+} + 2\mathsf{H}_2\mathsf{O} \xrightarrow{} \mathsf{MOH}^{(\mathsf{b}-1)+} + \mathsf{H}_3\mathsf{O}^+$

Z²r⁻¹ vs. pK_{a1} (roughly inverse relationship)

where Z is the numerical value of the charge, r is the ionic radius in nm, and pK_{a1} is the pH at which the aquo complex is present with half in the fully protonated form and half having lost a single proton

Table 13.1 selected m	Values of Z^2/r etal ions	(units are n	m^{-1}) and pK_{a1}	for aquo comp	lexes of
Metal ion	$Z^2 r^{-1} / nm^{-1}$	pK _{a1}	Metal ion	$Z^2 r^{-1} / nm^{-1}$	pK _{a1}
Na ⁺	8.6	14.48	Ni ²⁺	48	9.40
K^+	6.6	>14	Cu ²⁺	46	7.53
Be ²⁺	68	6.50	Zn ²⁺	46	9.60
Mg ²⁺	47	11.42	Cd ²⁺	37	11.70
Mn ²⁺	48	10.70	Hg ²⁺	34	3.70
Fe ²⁺	43	10.1	Al ³⁺	133	5.14
Co ²⁺	45.2	9.6	Fe ³⁺	115	2.19

-Waters of hydration surrounding M⁺ exist exclusively in protonated form throughout the entire pH range

-of M²⁺, deprotonation occurs more readily for smaller species due to the larger value of Z²/r. That is, in water with pH>6.5, Be(OH)⁺ will be more important than Be²⁺. The MgOH⁺ and CaOH⁺ species occur only at very high pH.

pK_a values taken from Yatsimirksii, K. B. and V. P. Vasil'ev, Instability Constants of Complex Compounds, Pergamon, Elmsford, N Y, 1960.

In each case, the radius used is for the the 6-coordinate high-spin metal aquo complex.

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 E.g. for Iron(III) species, consider the possibility of two deprotonation steps and the formation of a bridged dimer

$$\begin{bmatrix} (H_2O)_4Fe < O \\ O \\ O \\ H \end{bmatrix} Fe (OH_2)_4 \end{bmatrix}^{4^+}$$

Aluminium and some other metals are also known to form polynuclea r species. Taking into account the four species indicated in the equations below, we will calculate their concentrat ions in pure water at pH = 7.00. The relevant equilibria are as follows :

$$\begin{aligned} Fe(OH)_{3} &\leftrightarrow Fe^{3+}(aq) + 3OH^{-}(aq) & \mathrm{K}_{\mathrm{sp}} = 9.1 \times 10^{-39} \ (13.3) \\ Fe^{3+}(aq) + 2H_{2}O &\leftrightarrow FeOH^{2+}(aq) + H_{3}O^{+}(aq) & \mathrm{K}_{\mathrm{a1}} = 6.5 \times 10^{-3} \ (13.4) \\ FeOH^{2+}(aq) + 2H_{2}O &\leftrightarrow Fe(OH)_{2}^{+}(aq) + H_{3}O^{+}(aq) & \mathrm{K}_{\mathrm{a2}} = 3.2 \times 10^{-4} \ (13.5) \\ 2Fe^{3+}(aq) + 4H_{2}O &\leftrightarrow Fe_{2}(OH)_{2}^{4+}(aq) + 2H_{3}O^{+}(aq) & \mathrm{K}_{\mathrm{ad}} = 1.3 \times 10^{-3} \ (13.6) \end{aligned}$$

Chapter 13. Metals in the hydrosphere 13.1 Aquo complexes of metals

Note that the waters of hydration associated with the iron are not shown. Using the first reaction, 13.3:

$$[Fe^{3+}][OH^{-}]^{3} = K_{sp}$$
$$[Fe^{3+}][10^{-7.00}]^{3} = 9.1 \times 10^{-39}$$
$$[Fe^{3+}] = 9.1 \times 10^{-18} \text{ mol } L^{-1}$$

Using the second reaction, 13.4:

$$\frac{\text{FeOH}^{2+}][\text{H}_3\text{O}^+]}{[\text{Fe}^{3+}]} = 6.5 \times 10^{-3} \text{ mol } \text{L}^{-1}$$

Using the value of [Fe³⁺] calculated above:

$$[FeOH^{2+}] = \frac{6.5 \times 10^{-3} \times 9.1 \times 10^{-18}}{1.0 \times 10^{-7}}$$
$$= 5.9 \times 10^{-13} \text{ mol } \text{L}^{-1}$$

Similar calculations are done to determine the equilibrium concentrations of the two additional species:

$$[Fe(OH)_{2}^{+}] = 1.9 \times 10^{-9} \text{ mol } L^{-1}$$
$$[Fe_{2}(OH)_{2}^{4+}] = 1.1 \times 10^{-23} \text{ mol } L^{-1}$$

13.2 Classification of metals. Traditional classifications of metals

- Classification of metals: type A, type B, and transition metals
- Type A metal ions:

-ions with inert gas (d⁰) electronic configurations, characterized by spherical symmetry and low polarizability

-stability is positively related with Z^2/r (the (charge)²/radius ratio) for both the metal ion and the ligand species, therefore

-properties are:

1) O- or F-containing ligands are preferred to sulfur and higher halides, and hence form important soluble aluminium species, e.g. $AI(H_2O)_5(OH)^{2+}$ and $AI(H_2O)_4F_2^+$. They form weak complexes with oxyanions such as $SO_4^{2^-}$, NO_3^{-} , and oxygen containing functional groups (e.g. –COOH, =C=O)

2) May form insoluble OH⁻, CO₃²⁻ or PO₄³⁻ compounds, e.g. CaCO₃, AIPO₄

3) complexes with OH^{-} are more stable than those with HS^{-} or S^{2-} .

4) complexes with Cl⁻, Br⁻, and l⁻ tend to be weak

5) complexes with H_2O are more stable than those with NH_3 or CN^2

13.2 Classification of metals. Traditional classifications of metals

Type B metal ions:

-ions with nd¹⁰ and nd¹⁰(n+1)S² type electronic configurations, characterized by readily distorted electronic distributions, I.e. showing high polarizability:

-covalent bonding plays a role in complex formation, and Major factor affecting complex stability (β_f) is the ability of the metal to accept electrons from the ligand, i.e electronegativity (en) of both metal and ligand donor atom is an important factor.

-properties are:

1) generally form more stable complexes than type A metal

2) complex stability is in the order of $I^- > Br^- > CI^- > F^-$: this is the reverse of the situation observed with type A metals

3) N containing ligands form more stable complexes than O containing ligands. S or organosulfides form common and stable complexes

4) complexes with C, e.g. organometallic complexes (CH₃Hg⁺ and (CH₃)₂Hg) are observed

13.2 Classification of metals. Traditional classifications of metals

- Transition metal cations:
 - -ions with nd^{x} (0 < x < 10) electronic configurations
 - -properties are:
 - 1) exhibit intermediate properties between those of the type A and type B classes
 - 2) electrostatic factors play a role in determining stability of borderline metals. Because of increasing Z^2/r ,

13.2 Classification of metals. Environmental classifications of metals



- **Fig. 13.2** Classification of some metals of environmental importance. (Redrawn from Nieboer and Richardson, 1980.) Subdivisions based on the traditional, Ahrland *et al.*, and Pearson classifications are indicated by the horizontal lines. Stability of complexes increases with increasing ionic and/or covalent index, as shown by the arrow.
- Covalent index, X_m²r, (X_m=metal ion electronegativity, r=ionic radius of metal) reflects the ability of the metal to accept electrons from a donor ligand, and differentiate b/w type A, borderline and type B metals
- Ionic index, Z²/r, measures the possibility of ionic bond formation

13.2 Classification of metals. Environmental classifications of metals

Table 13.2 Principal aqueous species of environmentally important metal ions. (Only inorganic species are considered)

	pH = 4		pH = 7		pH = 10	
	oxidizing environment	reducing environment	oxidizing environment	reducing environment	oxidizing environment	reducing environment
Sodium	Na ⁺	Na ⁺	Na ⁺	Na ⁺	Na ⁺	Na ⁺
Potassium	K ⁺	Κ+	Κ+	K ⁺	Κ+	K+
Magnesium	Mg ²⁺	Mg ²⁺	Mg ²⁺ , MgSO4 (sw)	Mg ²⁺ , MgSO4 (sw)	Mg ²⁺	Mg ²⁺
Calcium	Ca ²⁺	Ca ²⁺	Ca ²⁺ , CaSO ₄ ⁰ (sw)	Ca ²⁺ , CaSO ₄ ⁰ (sw)	Ca ²⁺	Ca ²⁺
Aluminium	Al ³⁺ , AlOH ²⁺	Al ³⁺ , AlOH ²⁺	Al(OH) ⁺ ₂ , Al(OH) ⁰ ₃ ,	Al(OH) ⁺ ₂ , Al(OH) ⁰ ₃ ,	Al(OH) ⁻ ₄	$AI(OH)_4^-$
•			$AI(OH)_{4}^{-}$ (sw)	$AI(OH)_4^-$ (sw)		
Vanadium	H ₂ VO ₄ , VO ₂	V0 ²⁺	H ₂ VO ₄ , HVO ₄ ²⁻ , V ₁₀ O ₂₈ ⁶⁻	VO ²⁺	VO ₄ ³⁻	
Chromium	HCrO₄	CrOH ²⁺	HCrO ₄ , CrO ₄ ²⁻	CrOH ²⁺ , Cr(OH) ₂ ⁺	CrO4	$Cr(OH)_4^-$
Manganese	Mn ²⁺	Mn ²⁺	MnO ₂ , MnCl ⁺ (sw)	Mn ²⁺ , MnCl ⁺ (sw), MnSO ₄ (sw)	MnO ₂ ⁰	MnCO ₃
Iron	FeOH ²⁺ , Fe(OH) ⁺ ₂	Fe ²⁺	$Fe(OH)_3^0$	Fe ²⁺ , FeCO ₃ ⁰	$\operatorname{Fe}(\operatorname{OH})_4^-$	FeOH ⁺ , Fe(OH) ₂ ⁰
Cobalt	Co ²⁺	Co ²⁺	Co ²⁺ , CoCO ₃	CoCO ₃	Co ₃ O ₄	CoCO ₃

	pH = 4		pH = 7		pH = 10		
	oxidizing environment	reducing environment	oxidizing environment	reducing environment	oxidizing environment	reducing environment	
Nickel	Ni ²⁺ , NiSO ₄	Ni ²⁺	Ni ²⁺ , NiHCO ₃ ⁺ , NiCl ⁺ (sw)	Ni ²⁺ , NiHCO ₃ ⁺ , NiCl ⁺ (sw)	NiOH ⁺ , Ni(OH) ⁰ ₂ , NiCO ₃	NiOH ⁺ , Ni(OH) ⁰ ₂ , NiCO ₃	
Copper	Cu ²⁺	Cu ²⁺	Cu ²⁺ , CuOH ⁺ , CuHCO ⁺ ₃ , CuCl ⁺ (sw)	Cu ²⁺ , CuOH ⁺ , CuHCO ⁺ ₃ , CuCl ⁺ (sw)	$Cu(OH)_{2}^{0},$ $Cu(CO_{3})_{2}^{2-}$	$Cu(OH)_{2}^{0}, Cu(CO_{3})_{2}^{2-}$	
Zinc	Zn ²⁺	Zn ²⁺	Zn ²⁺ , Zn(OH) ⁰ ₂ , ZnCl ⁺ (sw)	Zn ²⁺ , Zn(OH) ⁰ ₂ , ZnCl ⁺ (sw)	$Zn(OH))_2^0$	$Zn(OH))_2^0$	
Molybdenum	HMoO ₄		HMoO ₄		HMoO_4, MoO_4		
Lead	Pb ²⁺ , PbSO₄	Pb ²⁺	Pb ²⁺ , PbOH ⁺ , PbHCO ₃ ⁺ , PbCl ⁺ (sw), PbSO ₄ ⁰ (sw)	Pb ²⁺ , PbOH ⁺ , PbHCO ₃ ⁺ , PbCl ⁺ (sw)	Pb(OH) ₂ , PbCO ₃ , Pb(CO ₃) ₂ ²	Pb(OH) ₂ , PbCO ₃ , Pb(CO ₃) ₂ ²	
Mercury	HgOH ⁺ , Hg(OH) ⁰ ₂ , HgCl ⁰ ₂	Hg⁰	$Hg(OH)_{2}^{0}, HgCl_{2}^{0}, HgCl_{4}^{2-}$ (sw), $HgCl_{3}^{2-}$ (sw)	Hg⁰	Hg(OH) ⁰ ₂	Hg⁰	

Sulfate, chloride, and carbonate in concentrations which approximate those found in average river water are assumed to be present in the water. The metal concentrations are also assumed to be in the range of those found in 'normal' water. Some neutral species such as $Fe(OH)_3$ and MnO_2 are highly insoluble and will be present as colloids even when the metal concentration is very small. The notation (sw) indicates that this additional species is present in sea water. Note that sea water pH is approximately 8.

Coordinated water molecules are not included in the formulae.

Chapter 13. Metals in the hydrosphere 13.2 Classification of metals. Complexes with humic materials

Example of HMs and their complexation with metal ions



Fig. 13.3 Examples of humic material functional groups available for complexation reactions. Structures c (phthalate) and e (salicylate) are thought to be particularly important players in chelate formation processes.



13.2 Classification of metals. Complexes with humic materials

- Factors influence the extent of complexation
- 1) nature of the metal ion: the ionic index and the covalent index (see Fig.13.2)
- 2) Ambient solution pH: the lower pH, the lower tendency of complex formation
- 3) Ionic strength: the ability of HM to react with transition metals is inversely related to solution ionic strength. Two reasons for this: competition for ligand sites from the cations (esp. alkaline earth cations) which contribute to the increased ionic strength, and availability of anions (like Cl⁻, SO₄²⁻, and HCO₃⁻) to react with metals, thus inhibiting metal-humate reactions
- 4) Availability of functional groups (K_f': conditional stability const. at specified pH)

Table 13-3 Conditional stability constants (pH 5.0) for soluble fulvic acids and selected metals							metals	
	Mg ²⁺	Ca ²⁺	Mn ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Pb ²⁺
K' _f	1.4x10 ²	1.2x10 ³	5.0x10 ³	1.4x10 ⁴	1.6x10 ⁴	1.0x10 ⁴	4.0x10 ³	1.1x10 ⁴
Schnitzer,	Schnitzer, M. and S. U. Khan, Soil Organic Matter, Elsevier, Amsterdam; 1978.							

Consider water (pH=5, 85 μ g/L (1.44 μ mol/L) of Ni, 8 mg/L of FA, functional groups of FA = 5 mmol/g) Calculate the conc. of complexed Ni.

13.2 Classification of metals. Complexes with humic materials

Consider water (pH=5, 85 μ g/L (1.44 μ mol/L) of Ni, 8 mg/L of FA, functional groups of FA = 5 mmol/g) Calculate the conc. of complexed Ni.

$$Ni + FA \rightarrow NiFA$$
 (13.8)

For the reaction, the conditional stability constant is

$$K'' = \frac{[\text{NiFA}]}{[\text{Ni}_{u}][\text{FA}_{u}]} = 1.6 \times 10^{4}$$
(13.9)

In this formulation, $[Ni_u]$ refers to the total concentration of all soluble nickel species that are not complexed with fulvic acid and $[FA_u]$ is similarly the concentration all of the fulvic acid not complexed with nickel. The latter concentration is expressed in terms of functional groups available for complexation and we are assuming that no other metals are present to compete for these sites.

Since the ligand is available in large excess, we can make the approximation that $C_{FA} = [FA_u] = 4 \times 10^{-7} \text{ mol L}^{-1}$. The total concentration of nickel is $1.44 \,\mu\text{mol L}^{-1}$. Let the value of uncomplexed nickel, $[Ni_u] = u$.

$$\frac{(1.44 \times 10^{-6} - u)}{u \times 4.0 \times 10^{-7}} = 1.6 \times 10^{4}$$

Therefore

$$u = [Ni_u] = 8.8 \times 10^{-7} \text{ mol } L^{-1}$$

and

$$[NiFA] = 5.5 \times 10^{-7} \text{ mol } L^{-1}$$

Chapter 13. Metals in the hydrosphere 13.3 Three metals - their behavior in the hydrosphere: Ca



Fig. 13.4 Major components of the calcium environmental cycle.

Chapter 13. Metals in the hydrosphere 13.3 Three metals - their behavior in the hydrosphere: Cu



Fig. 13.5 The principal features of the environmental cycle for copper.

- Global avg. abundance=63 μg/g in the Earth's crust.
- A borderline metal, having a good ability to form complexes with a variety of ligands, particularly N containing ligands.

Chapter 13. Metals in the hydrosphere 13.3 Three metals - their behavior in the hydrosphere: Hg



- Global avg. abundance=89 ng/g in the Earth's crust.
- Found in element form or combined with S or methyl groups.
- Important contribution from gas-phase species

Fig. 13.6 Major components of the environmental cycle of mercury.

Chapter 13. Metals in the hydrosphere 13.4 Metal complexes with ligands of an anthropogenic origin

Some complexing agents that are released as effluents into water bodies include the following:

- ammonia-resulting from the decay of nitrogen-containing organic wastes;
- sulfide, sulfite, and sulfate—discharged from pulp and paper mills, depending on the processes used;
- phosphate—a constituent of some detergents and therefore present in municipal waste water; also released from agricultural run-off where phosphate fertilizers have been used;
- cyanide—used in various industrial processes including extraction of gold from ore minerals;
- EDTA (ethylenediaminetetraacetic acid)—used for industrial cleaning, in the photographic, textile, and paper industries, and in detergents in some countries such as Germany;
- NTA (nitrilotriacetic acid)—a detergent builder employed in some countries such as Canada and several countries in northern Europe.

The behaviour of NTA in water provides an interesting case study of the effect of introducing a human-produced complexing agent into natural water. Where its use is permitted, NTA is present in detergents at a concentration of about 15% by mass in order to act as an efficient binder for calcium and other ions present in water. Sequestering the metals improves the action of the surfactants in the detergent. The structural formula of NTA (molar mass = 191.8 daltons) is



As can be seen from the formula, NTA is a triprotic carboxylic acid; the acid dissociation constants are $pK_{a1} = 1.66$, $pK_{a2} = 2.95$, and $pK_{a3} = 10.28$.

Chapter 13. Metals in the hydrosphere 13.4 Metal complexes with ligands of an anthropogenic origin



Fig. 13.7 The tetrahedral complex formed between nitrilotriacetic acid (NTA) and copper.

Metal ion	Log K _f	Metal ion	Log K _f
Mg ²⁺	5.47	Mn ²⁺	7.46
Ca ²⁺	6.39	Cu ²⁺	12.94
Fe ²⁺	8.82	Zn ²⁺	10.66
Fe ³⁺	15.9	Pb ²⁺	11.34