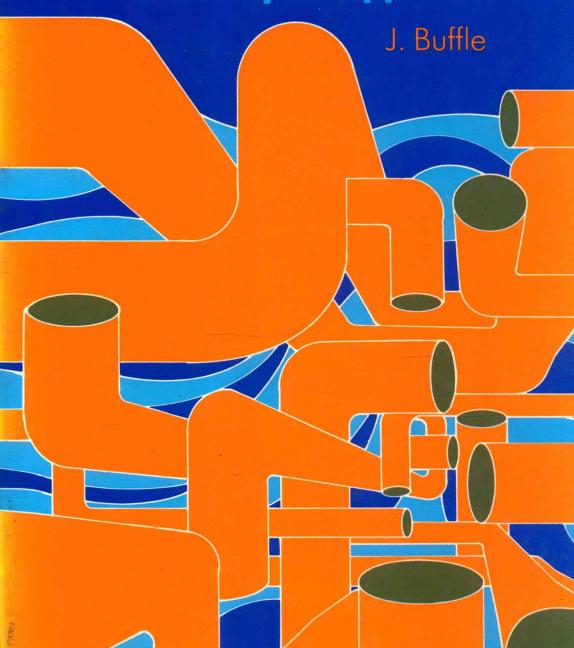# COMPLEXATION REACTIONS IN AQUATIC SYSTEMS

an analytical approach

J. Buffle

COMPLEXATION REACTIONS IN AQUATIC SYSTEMS:
An Analytical Approach

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This book discusses the chemical reactivities (and ecological implications) of metal ions with all complexants in aquatic systems, i.e. waters, sediments and soil waters. It highlights the reactions with chemically ill-defined, complicated and heterogeneous components which play a major role in metal regulation, and gives a critical comparison of the properties of the various natural heterogeneous complexing systems, and of the analytical approaches used to study them.

The book classifies aquatic complexing agents and metals as a function of their concentration and properties, discussing their environmental role and behaviour. It compiles the properties of natural organic matter in soils, waters and sediments with particular emphasis on the nature and contents of the various complexing sites. It reviews the properties of the most important natural complexants, offering the data necessary for a critical comparison.

Theoretical models for interpreting complexation experimental data with heterogeneous systems are reviewed and compared, and a detailed discussion of the analytical methods used for complexation measurements, with a review of associated problems, is provided. There is much quantitative information, including 150 tables of natural compound data which are collected "under one roof" for the first time.

Readership: Analytical chemistry, environmental chemistry, water chemistry, biochemistry, clinical chemistry, limnology, oceanography, inorganic chemistry, soil and sediment science, hydrology, pollution science, etc.

Jacques Buffle works in the Department of Inorganic, Analytical and Applied Chemistry at the University of Geneva, Switzerland, where he has been Maître d'Enseignement et de Recherche since 1982. He has also, since 1982, been Invited Professor at INRS-Eau, University of Quebec, Canada. Prior to this he was Charge de Recherche and Charge de Cours, at the University of Geneva (1969–81). He was awarded Diplomas in Chemistry and Biochemistry (1966), a Ph.D. in Analytical Chemistry (1969), and a Diploma in Computer Calculation (1971), all from the University of Geneva. He was a Member and Chairman of the Sub-committee on Environmental Trace Analysis for the IUPAC Commission on Electroanalytical Chemistry (1981–87), and is Member Chairman of the Divisional Sub-committee on Environmental Analytical Chemistry.

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Preface

THE IMPORTANCE OF CHEMICAL REACTIVITY MEASUREMENTS IN NATURAL WATERS

In natural waters — as in all solution environments — the bare metal ions are in continuous search of a partner. All metal cations in water are hydrated. The co-ordination reactions in which metal cations participate are exchange reactions in which the co-ordinated water molecules become exchanged for some preferred ligands. The barest of the cations is the proton. The scenario of multi-metal–multi-ligand binding in natural water systems can be complicated: the ligands are either simple or polymeric solutes with suitable donor atoms, or functional ligand groups on surfaces of inorganic or organic particles. The particle–water interface, above all the biota–water interface, plays a dominating role in regulating the concentration of most reactive elements in natural waters and in the coupling of various hydrogeochemical cycles. The more reactive an element is with lake or ocean particles, i.e. the higher its affinity for the donor atoms of the particle surface in comparison to its affinity for solute ligands, the more it will be bound to particles and the more rapidly will it be removed and the shorter will be its residence time. What is the role of 'dissolved' organic macro-molecules, particularly the humic and fulvic acids in natural waters? First, because of their polyfunctional properties they are ideal metal-complex formers, regulating the free ion concentration (more rigorously, pMe, especially pCu) which in turn determines the physiological conditions for the growth of algae and other micro-organisms. Secondly, they assist in photochemically induced processes, for example reducing iron(III) and manganese(IV) oxides to which

they are surface-bound, thus making the essential Fe(II) and Mn(II) available to micro-organisms. These examples suggest the complexity, but also the necessity, of correct determination and interpretation of metal reactivity in natural waters, for good control of our environment.

Jacques Buffle's task in writing this treatise on the complexation reactions in natural waters was not easy. In discussing the different approaches to the interpretation of complexant behaviour, he has the courage to confront the reader ultimately with the full complexity of real natural water systems, characterized not only by molecular level chemical heterogeneity but also by natural structural heterogeneity at the macroscopic scale. His skilful explanations of various approaches to transforming raw experimental data into quantitative representation of the distribution of complexing properties in real systems are especially useful to those students and researchers who are eager to make their own measurements and find quantitative interpretations. Those of us who share an interest in and a concern for natural waters are indebted to Jacques Buffle for having written this book, which will bring us a great step closer to a better understanding of a complex medium, the natural waters.

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ANALYTICAL CHEMISTRY AND SPECIATION

Ever since completing his doctoral thesis in 1969 on the anodic stripping voltammetric determination of iron(III) [which also included pioneering studies of hydroxo-complexes of iron(III) in dilute aqueous media] and the measurements he started more than ten years ago on the complexation properties of humic and fulvic acids, Jacques Buffle's interest has been the study of the nature and physicochemical properties of aquatic organic and inorganic macromolecules and colloids, their interactions with trace metals and their role in controlling metal bioavailability. Each of these studies necessitated development of new analytical methods and establishment of theoretical models in order to enable determination of inert and labile species in aquatic systems and subsequent interpretation of their interactions with heterogeneous natural complexants. One of the objectives of his book is, therefore, to show us how, as analysts, we should go about choosing analytical techniques and data-interpretation methods which are appropriate to these immensely complicated systems.

The material presented in Jacques Buffle's book should teach us that the days are long gone when analytical chemistry could be regarded as simply the servant of other branches of chemistry. This notion that analytical chemistry is an academic chemical discipline of minor importance originated with those people who forgot that without analysis, our understanding of chemistry would never have come into existence. Analytical chemistry is certainly not merely 'chemical analysis', i.e. a discipline dealing only with technical aspects, such as 'Instrumentation', 'Automation' and recently

'Robotics'. The analyst must also be equipped with a broad and sound knowledge not only of chemistry but also, for example, of physics, biology, electronics and statistics. In many instances the analyst will be confronted with new kinds of samples, unexpected and complicated combinations of elements, sample instability, and inhomogeneity of species, requiring that he think long and hard before deciding on the best approach to take in solving the problem at hand, problems which are found not only in industry and pure research but also and even more in our environment. This implies specific ways of thinking, which supports the contention that modern analytical chemistry, despite its apparent multidisciplinary character, is a unified and independent scientific discipline, standing alongside the other branches of chemistry in the general development of that science. With the rapid progress of technology in general, it is constantly necessary to see that the development of chemistry does not irrationally follow technology, but is orientated toward the well-being of both mankind and his environment. It is one of the important tasks of the analytical chemist to help to maintain such an equilibrium, since his broad-ranging knowledge will make him especially qualified to do this competently and efficiently.

One of the more important general concerns of analytical chemistry is the qualitative and quantitative characterization of matter and interpretation of the results obtained. This concern is of prime importance in the field of environmental analytical chemistry. Indeed, characterization of the properties of particular chemical species is a virtual necessity when studying environmental problems such as those encountered in natural waters. Determination of only the total concentration of specific elements present in this type of sample is frequently of little value, knowledge of the chemical forms being of much greater importance, since only knowledge of speciation aids in our understanding of the processes regulating the uptake and action of metal compounds and in elucidating their critical pathways in the environment and living organisms. What is needed at present is development of new analytical techniques and procedures satisfying the demands of speciation analysis, i.e. the determination of the individual physicochemical forms of the element, which together make up its total concentration in a sample, as well as their properties.

Jacques Buffle, in his book, presents his own wide experience acquired in this field. Saying that, I am sure that readers will appreciate the contents and, like me, learn something new about analytical chemistry.

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Foreword

This book, in attempting to combine various aspects of analytical chemistry and the chemistry of natural waters, employs an approach requiring aquatic phenomena to be viewed from perspectives and in frames of mind which are different and, at times, quite removed from one another. In this regard this book has richly profited from the experience communicated by numerous persons expert in a variety of domains: geology, biology, biochemistry, electrochemistry, and colloidal, inorganic and analytical chemistry.

Unfortunately, it is not possible here to thank by name all of the people who have contributed, from near or far, to the realization of this book. I wish, however, especially to thank W. Haerdi and W. Stumm. The ideas which are developed in the following material to a large degree rely, on the one hand, on the frame of mind necessary to apply instrumental analytical methods to complex natural media, a field that W. Haerdi has always been bent on promoting, and, on the other hand, on the utilization of rigorous physicochemical concepts for interpretation of reactions occurring in aquatic media, a domain to which W. Stumm has contributed greatly in establishing the necessary foundations. Their experience and support in these complementary domains have been very precious to me and this book owes much to their open mindedness and their friendship.

I would like equally to thank the numerous persons, such as P.G.C. Campbell, Z. Galus, D.S. Gamble, G.G. Leppard, J. Mallevialle, P.W. Schindler, M. Schnitzer, A. Tessier, P. Valenta, H.P. Van Leeuwen, A. Zirino, and many

others as well, whom space, unfortunately, does not allow me to mention and who, to differing degrees but always with ready availability, allowed me to profit from their experience during numerous and friendly exchanges. This book also owes much to all of the people, doctoral students, technicians and post-doctoral colleagues, with whom I have had the pleasure of collaborating directly during some 15 years and who have agreed to embark on studies into the intricacies of nature and the role played by the reactions of inorganic ions in aquatic media, most often with poorly characterized compounds. Through the experience that each one of them has brought, they have all participated in the realization of this book. Particular thanks go to S.P. Kounaves and R.S. Altmann, for their co-operation and availability during their work in translating Chapters 1–7 and 8–10 respectively, and to R. Baudat for his assistance in preparing the figures. The final version of this book owes much to the remarks and competence of R.S. Altmann, as well as to those of A. Balikungeri, N. Parthasarathy, M.L. Tercier and A. Tessier who were willing to reread certain parts of the manuscript.

Lastly this book also owes much to the enthusiasm communicated by my father, J. Ph. Buffle, concerning the numerous aspects of environmental sciences, and to my wife, Reyne, and my son, Marc-Olivier, whom I wish to thank especially for the patience they have shown during the entire drafting of this book and for having accepted in good humour the restrictions therefore imposed on family life.

J. Buffle

List of Symbols

1 QUANTITATIVE PARAMETERS

1.1 Latin alphabet symbols

A	Surface area
A_s	Specific surface area (per unit weight)
$(\tilde{C}_c), C_c$	(Average) complexing capacity
c_M	Concentration of metallic M in Hg or in amalgam electrode ($[M^0]$ is also used for this parameter)
$c_{M,0}(t)$	Concentration of metallic M in Hg or amalgam electrode at $x = 0$ and time t
D_x	Diffusion coefficient of compound X
E	Potential imposed or measured on an electrode
$E_{Q=0}$	Potential of zero charge on an electrode
E_0	Standard redox potential (for redox couples) or constant parameter characteristic of membrane electrodes (ISE)
$E_i, E_f, E_e, E_a:$	Initial, final, electrolysis, and adsorption potential in voltammetric methods
$\bar{E}$	Average interaction energy between sites in a polyfunctional complexant
f	Fraction of polyelectrolyte deprotonated sites or frequency of alternating potential imposed in ac polarography
F	Faraday constant (96485 C)
^jF	Fraction of sites j with respect to the total number of sites in a polyfunctional complexant

h	Number of protons liberated by complexation of M
i	Faradaic current in voltammetric methods
i_c	Capacitive current in voltammetric methods
i_t	$i_c + i$
i_e	Pre-electrolysis (deposition) current in ASV
j, j_A, j_M	Current density $(= i/A)$: total, or due to anion A or cation M respectively
J_X	Flux of compound X through an interface
K	Equilibrium constant
$^{ij}K_{lm}^{th}$	Thermodynamic complexation equilibrium constant for reaction between m cations ^iM and l ligand ^jL
K_{int}	Intrinsic equilibrium constant (corrected for 'secondary' effects)
K'	Apparent equilibrium constant, valid at constant pH
$K, \bar{K}, \tilde{K}$ or $K', \bar{K}', \tilde{K}'$	For a polyfunctional complexant: differential equilibrium function (K, K'), average equilibrium function $(\bar{K}, \bar{K}')$, or average equilibrium quotient $(\tilde{K}, \tilde{K}')$
$K_{1,j}^{pot}$	Selectivity coefficient of membrane electrode
l	Number of ligand molecules L in a complex $M_m L_l$, or thickness of the mercury film in voltammetric methods
m	Number of M cations in a complex $M_m L_l$
n	Maximum number of ligands bonded to M, or number of electrons exchanged in a redox reaction
$\bar{n}$	Average coordination number of M in a series of complexes $ML_1, \ldots ML_n$
N	Number of complexing sites per mole of a well-characterized complexant
$\tilde{N}$	Average value of N for a polyfunctional homologous complexant
$p(K')$	Probability density function of finding a site L forming ML complexes with stability constant K'
$p'(K')$	$= p(K')/2.303$
$(\bar{Q}), Q$	Overall (average) number of charges per gram of complexant
Q_+, Q_-	Number of positive and negative charges per gram of complexant
q	Charge of a polyelectrolyte P (in coulomb/mole of P)
r	Radius of a spherical particle or Hg drop
r_G	Gyration radius of a macromolecule
r_h	Hydrodynamic radius of a particle
R_X	Overall retention coefficient of a compound X by membrane ultrafiltration
S	Slope $(= 2.3\, RT/zF)$ of the calibration curve of a membrane electrode (ISE)
t	time, or average age (e.g. of a sediment)

t_e, t_w, t_a	Pre-electrolysis, waiting and adsorption time, respectively, in voltammetric methods
t_p	Pulse duration in pulse polarography
x	Distance (in particular from the electrode or membrane surface)
$(\tilde{Z}), Z$	(Average) number of electronic charge per mole of complexant
Z_r	Residual charge in the condensation theory of Manning
z	Number of electronic charge (algebraic) on an ion
$[X], \{X\}$	Molar concentration and activity of the compound X (subscript 0 refers to the corresponding values at distance $x = 0$ from the complexing site or the electrode surface)
$[X]_t$	Total concentration of X, irrespective of its chemical form
$\{P\}$	Concentration of P expressed in g/l.

1.2 Greek alphabet and other symbols

α	Degree of complexation of a metal ion (^iM: $^i\alpha$) or a ligand (^jL: $^j\alpha$)
$^i\alpha_0, {}^j\alpha_0$	Fractions of ^iM or ^jL in the free form, with respect to the corresponding total concentration
$(\tilde{\beta}), \beta$	(Average) cumulative complexation equilibrium constant (subscripts and superscripts as for K)
γ_x	Activity coefficient of compound X
γ	Surface tension at the Hg–solution interface in electrochemistry
Γ_x	Surface concentration of the adsorbed compound X
$\delta_{ML}, \delta_M, \delta_R$	Diffusion layer thickness of ML (δ_{ML}) and M(δ_M) in solution and of M^0 (δ_R) in Hg electrode
ϵ	Dielectric constant
η	Viscosity
η_0	$= \lambda/\lambda_0$ (see below)
$^j\theta$	Probability of occupation of a single site j
$^j\bar{\theta}$	Average degree of occupation of all sites j of a polyfunctional complexant
$\bar{\theta}$	Average overall degree of occupation of sites
λ	Degree of site protonation in the absence of secondary effects (see definition in Section 5.3.1.3)
λ_0	As above, but in the presence of secondary effects
μ_0	$= [M]_0/[M]$ = ratio of M concentration at the complexing site to that in the bulk solution, for complexation by homologous complexants
μ	Thickness of the reaction layer at the electrode surface in electrochemical methods

$\bar{v}$	Average overall degree of site occupation, expressed in moles of bound M per mole of polyfunctional complexant P
$\bar{v}^*$	As above but concentration of P expressed in g/l.
ρ	Density
$\bar{\rho}$	(with subscripts): Average parameter related to interaction energy between sites in a polyfunctional complexant
σ	Specific charge of a polyelectrolyte (coulomb per unit surface area)
σ_x	Retention coefficient of a compound X in ultrafiltration
φ	Electric potential at one point of the circuit in electrochemical methods
$\Delta\varphi$	Potential difference between the electrode and the solution
$\Delta\varphi^i, \Delta\varphi^e$	Potential differences between the electrode and the solution at the internal and external surfaces respectively
$\phi(\bar{\theta})$	Function relating the dependency of the binding energy of an ion M by a polyfunctional ligand P to the degree of site occupation
ψ_x	Potential in solution at a distance, x, from a charged surface
τ_H	Acid—base buffer capacity
τ_X	Residence time of compound X in a reservoir
$\tau_{1/2}$	Half-reaction time
ω	Rotation speed of a rotating disc electrode

2 CHEMICAL COMPOUNDS

AA	Amino-acids
AntOM	Anthropogenic organic matter
AOM	Aquagenic organic matter (formed *in situ* in water bodies)
AROM	Aquagenic refractory organic matter
—COOH	Carboxylic sites
DIM	Dissolved inorganic matter
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
E	Any element of the periodic table
FF, (FA)	Fulvic fraction (acid)
HF, (HA)	Humic fraction (acid)
L	Ligand or complexing site ($^j L$ = ligand or site number j)
$L_H, (L_S)$	Hard (soft) ligand or complexing site
LDOC	Labile dissolved organic carbon
LOC	Living organic carbon
M	Free, hydrated, metal ion or, more generally, free compound to be complexed by a ligand L ($^i M$ = free ion or compound number i)
ML	Complex formed between M and L
N_{org}	Organic nitrogen
NOM	Natural organic matter

P	General symbol for homologous (often polyfunctional and polyelectrolytic) complexant
PIM	Particulate inorganic matter
POC	Particulate organic carbon
PON	Particulate organic nitrogen
POM	Pedogenic organic matter (Aquatic NOM with soil origin)
PROM	Pedogenic refractory organic matter
RDOC, (RPOC)	Refractory dissolved (particulate) organic carbon
ROM	Refractory organic matter
SOM	Soil organic matter
SedOM	Sediment organic matter
SDOC, (SPOC)	Slowly degraded dissolved (particulate) organic carbon
S_{org}	Organic sulphur
$\equiv S-OH$	$-OH$ sites at the surface of colloidal suspended particles
TA	Total acidity
TFAA	Total free amino-acids
TFFA	Total free fatty acids
TFMS	Total free monosaccharides
THAA	Total combined hydrolysable amino-acids
THFA	Total combined hydrolysable fatty acids
THMS	Total combined hydrolysable monosaccharides
TOM	Trifigenic (with peat origin) organic matter
TOC	Total (non-living) organic carbon
WFA, (WHA)	Water fulvic (humic) acids
$\phi-OH$	Phenolic sites