Atlas of Metal-Ligand
Equilibria in Aqueous Solution

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To
Coby
Edith
Annelies

*Put it before them briefly so they will read it,
clearly so they will appreciate it, picturesquely
so they will remember it and, above all, accurately
so they will be guided by its light.*

<div align="right">JOSEPH PULITZER</div>

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Foreword

Present-day theoretical treatments of metal–ligand equilibria owe much to Ringbom's *Complexation in Analytical Chemistry*. Since this book was published in 1963, many authors have found it useful to follow Professor Ringbom in his use of 'conditional constants' and 'side-reaction coefficients'. However, until now, in order to work with conditional constants it has been necessary to consult tables or carry out tedious calculations. I believe, therefore, that Dr. Kragten has done a great service for analytical chemists in producing this collection of plots of side-reaction coefficients for 45 metals in combination with 29 ligands, which give the necessary information at a glance. The accompanying plots of pM' against pH, which illustrate directly the areas of predominance of the various species and indicate the conditions under which hydroxides will precipitate and polynuclear hydroxo-complexes will form, also provide valuable information for the analyst. It is a great pleasure to be associated with the publication of this most useful addition to the analytical literature.

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M. R. MASSON
University of Aberdeen
</div>

2 August 1977

Author's Preface

There is increasing interest at the present time in making critical compilations of the equilibrium constants for metal–ligand complexes. Without such a compilation, the chemist is faced with a mass of confusing and possibly imprecise data. Original papers often contain insufficient information about the experimental set-up, the temperature, the ionic strength, the age and exact nature of any solid phase, etc., and the reader may not be able to criticize the data adequately. Thus, critical compilations satisfy an important need in analytical and coordination chemistry.

Nevertheless, only limited use is made of these critical compilations. The complexity of the equilibrium systems means that it is not easy to obtain – directly from the constants – a clear insight into the behaviour of the metal ions under the various experimental conditions possible. Usually, an intermediate graphical representation is used as an aid to understanding, but the extensive calculations and plotting of graphs necessary for each metal–ligand combination are tedious and time-consuming. Moreover, if someone does perform the necessary calculations, he will restrict himself to his own particular problem, and this in turn means that the few results available in the literature are not generally useful. Thus we can see that a gap exists between the data in the literature and daily laboratory practice, and that it should be filled in such a way that the information is readily available in an easily accessible and generally applicable form. In compiling this Atlas, my aim has been to fill this gap and to help the chemist working in industrial and research laboratories to solve everyday problems.

Although the greatest care has been taken in selecting the constants to be used, it was impossible to check each one for reliability. Specialists in a particular field may well be able to detect errors in the plots relating to their own speciality, and I hope that anyone who does detect such an error will not hesitate to contact me, so that I can incorporate the necessary correction in any future edition.

I am grateful to the copyright-holders, John Wiley and Sons, and to the authors, Dr. C. F. Baes Jr. and Dr. R. E. Mesmer, for permission to make use of data in *The Hydrolysis of Cations*.

I am greatly indebted to Mr Steven Arlman for his assistance in preparing the computer program, his stimulating input of ideas, his painstaking plot administration and his assistance in plot-scanning. Without him, the book could not have appeared for some years. I am grateful to the staff of the Physical Laboratory for giving me the opportunity to prepare this Atlas by allowing Mr Arlman and myself to have sufficient free time, and by supporting the work with a considerable proportion of the computer budget.

I thank Mr Joop van Loenen and the production staff of SARA (the Academic Computer Centre, Amsterdam) for their pleasant cooperation during the production of the computer plots, and for their patience in ensuring that the plots were of the high quality needed.

I wish to express my gratitidue to Mr A. Ph. Reynaert, whose practical experience, achieved by meticulous observation, was the inspiration for the Atlas, to Prof. Gerrit den Boef and Prof. Adam Hulanicki for their interest and encouragement, and to Mrs Mariet Mölders and Mrs Tineke Koster for their assistance in typing.

I am grateful to the Series Editors, Dr. R. A. Chalmers and Dr. Mary Masson, for their help in preparation of the manuscript, and my final thanks go to Felicity, Ellis and Clive Horwood for their enthusiastic cooperation, and for being such a friendly publishing family.

J. KRAGTEN

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CHAPTER 1

Introduction

It is unthinkable that anyone should attempt to describe the properties of metal ions in aqueous solution without considering hydrolysis reactions. Most cations hydrolyse in aqueous solution, because they form strong bonds with oxygen atoms, and because, as a result of the self-ionization of water, hydroxide ions are always present at concentrations which can vary over the unusually wide range of $10-10^{-14}$ M. With some metals the bonds with oxygen are so strong that the species $M(OH)_2^{n+}$ do not dissociate further even in concentrated strong acids. Such species are sometimes written as MO^{n+}, particularly when their exact composition is not known. In the calculations, the species MO^{n+} was treated as if it were a metal ion of valency n.

When other ligands are present in solution, there will be competition between the ligands, L, and the products of hydrolysis. A general formula for the final product is $M_a O_b (OH)_c (H_2 O)_d L_e H_f$. However, without forgetting the correct formula for the product, it is possible to express the reactions in simpler terms if hydroxide ions and hydrogen ions are considered to be the only ligands competing with L. (This is possible because O^{2-} and H_2O can be expressed in terms of OH^- and H^+.) In all cases of interest, this representation is adequate for our purposes.

We have studied the reactions of 45 metals with 29 ligands, and about 600 of the combinations turned out to be of real interest. Different methods of graphical presentation are possible, but since most workers are not interested in detailed information about the exact distribution of metal ions between the various possible metal–ligand and metal–hydroxide species, but want to be able to find out such basic things as the pH at which a hydroxide precipitates, the conditions for formation of polynuclear complexes, and the conditional constant for reaction of the metal with EDTA or DCTA, I decided to present two types of plots.

The concept of the side-reaction coefficient, first introduced by Schwarzenbach, was extensively used by Ringbom in his excellent monograph *Complexation in Analytical Chemistry* [1]. In the first type of plot, the side-reaction coefficient (α) for reaction of the metal ion with hydroxide and ligand is plotted against pH for various ligand concentrations.

The second type of plot is of pM' *vs* pH. Such plots illustrate the influence of metal–ligand complex formation on the regions where polynuclear hydroxo-complexes form and where hydroxide precipitates. The material is presented in such a way that the graphs for the separate metal–ligand combinations are superposable; the graph for a system containing more than one ligand can be composed from the graphs for the individual metal–ligand combinations.

In preparation of this Atlas, certain simplifying assumptions had to be made, and one of these was that the metal–ligand species are not polynuclear. In reality, binuclear and polynuclear species are formed in concentrated solutions with some metal–ligand combinations. If this is known to occur in solutions with pM' < 2, a warning, d, is given in the tabular index to indicate that the pM'–pH diagram may not be completely reliable when pM < 2. (See, for example, DTPA and citrate.) If such species are formed in more dilute solutions, no plots are given, or the ligand is not considered at all (e.g. dimercaptopropanol, BAL).

Some metal–ligand complexes have limited solubility. If the metal–ligand complex precipitates only in concentrated solutions, a warning, p, is given in the tabular index. If precipitation occurs in more dilute solutions, no plots are given (e.g. oxalates, fluorides) or the ligand is not considered at all (phosphate).

Another possibility that had to be neglected was the formation of mixed-ligand complexes.

The greatest care was taken in selecting values for the constants from the literature, and the computer output (plots and print-out) was double-checked against the original literature. Nevertheless, it must be realized that there is some uncertainty in the positions of the lines on the plots, and that the accuracy of their positions depends on the accuracy of the data used. Only data which seemed obviously unreliable have been rejected; the relevant combinations are marked U in the tabular index. Where there was some doubt, the data were still used to produce plots, in view of the likelihood of unsuspected errors in the rest of the data. It was impracticable to check the accuracy of the constants (there were more than two thousand) for all the metal–ligand combinations. However, in many cases, large errors in some of the constants lead to only relatively minor inaccuracies in the positions of the lines.

1.1   THE PLOTS: THEORY

1.1.1 Hydroxides

Hydroxide equilibria form the basis of all the plots, and in this section the formation of the various hydroxide species will be discussed. The influence of other ligands will be considered later.

The reaction scheme for hydroxide formation can be set out as below; for argument's sake the metal ion is supposed to be tervalent, M^{3+}.