



شبكة المعلومات الجامعية

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



شبكة المعلومات الجامعية
@ ASUNET

جامعة عين شمس

التوثيق الالكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
على هذه الأفلام قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأفلام بعيدا عن الغبار

في درجة حرارة من ١٥-٢٥ مئوية ورطوبة نسبية من ٢٠-٤٠%

To be Kept away from Dust in Dry Cool place of

15-25- c and relative humidity 20-40%



شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

وثائق لم ترد بلاصل

يصعب قراءة بعض الوثائق

METAL ION - α - AMINO ACID EQUILIBRIA IN SYNTHETIC SEAWATER

THESIS

Submitted to the Faculty of Science
Alexandria University
In partial fulfilment of the Requirements
for the Degree of M. Sc. (Chemistry)

BY

HANAN HAMED SHAKER ABD EL-HALIM

(B. Sc. 1988)
Research Assistant
National Institute of Oceanography & Fisheries

SUPERVISED BY

Prof. Dr. M. M. Osman

Professor of Analytical Chemistry
Faculty of Science
Alexandria University

Prof. Dr. M. F. Iskander

Professor of Analytical and Inorganic
Chemistry
Faculty of Science
Alexandria University

Dr. N. J. Lees-Gayed

Lecturer of Analytical and Inorganic
Chemistry
Faculty of Science
Alexandria University

Prof. Dr. H. I. Emarā

Head of Marine Chemistry
National Institute of Oceanography
and Fisheries,
Alexandria

Alexandria University
Faculty of Science

1994



To my mother
father
and brothers

NOTE

Besides the work carried out in this thesis, the candidate *Hanan Hamed Shaker* has passed successfully the following courses in partial fulfilment of M.Sc.degree:-

- 1- Inorganic Reaction Mechanisms
- 2- Symmetry and Group Theory
- 3- Instrumental Analysis
- 4- Chemical Equilibria
- 5- Electrochemistry
- 6- Chemical Kinetics and Reaction Mechanism
- 7- Thermodynamic in Solution
- 8- Solid State Chemistry
- 9- Quantum Chemistry
- 10- Polymer Chemistry
- 11- Organic Chemistry
- 12- Physical Organic Chemistry
- 13- German Language
- 14- Elementary Course in The Basic Language of Computer
- 15- Seminar and Oral Examination

Prof.Dr.M.M.Abd El Rahman

Head Of Chemistry Department

Contents

Acknowledgment

Abbreviations

Summary vi

1. Introduction

1.1 Speciation in Marine and Other Aquatic Environments 1

1.1.1 Speciation Analysis. 2

1.1.2 Equilibria in Model Water Systems 4

1.1.2.1 Artificial Seawater. 7

1.1.3 Thermodynamic Modelling of Aquatic Systems. 8

1.1.4 The Importance of Speciation Studies in Aquatic Systems ... 11

1.1.4.1 Environmental Pollution 11

1.1.4.2 Toxicity of Trace Metals 14

1.2 Solution Equilibria of Glycine and α -Alanine in Media

Simulating Seawater 17

1.2.1 pH Scale Employed in Equilibrium Studies 17

1.2.2 The Autoprotolysis Constant of Water 19

1.2.3 Equilibria of Glycine and α -Alanine 20

1.3 Aim of the Work 25

2 Experimental and Computational Methods.

2.1 Experimental Methods. 26

2.1.1 Potentiometric Titration Methods for Determining Protonation and Stability Constants 26

2.1.2 Composition of the Artificial Seawater 32

2.1.3 The Chemicals and their Purification. 34

2.1.4 Preparation of the Stock Solutions and Determination of their Concentrations 35

2.1.5 The Measurement Procedure 36

2.1.5.1 Preparation of the Solutions Titrated.	37
2.1.5.2 The Titration Procedure.	40
2.2 Computational Methods	42
2.2.1 Protonation and Stability Constants.	42
2.2.2 End Point Determination and Electrode Checks.	45
2.2.3 Gran Plots	46
2.2.4 Calibration of the Potentiometric System and Determination of the Autoprotolysis Constant of Water.	47
2.2.5 Computation of the Protonation and Stability Constants.	49
2.2.6 WSTD Program.	51
2.2.7 Calculation of the Distribution of Species for Protonation and Complex Formation Equilibria	52
3 Results and Discussion	
3.1 The Calibration Titrations	56
3.1.1 The Calibration Data, the Autoprotolysis Constant of Water and the Protonation Constant of the Sulphate Ion	56
3.1.2 Autoprotolysis Constant of Water	61
3.1.3 Protonation Constant of the Sulphate Ion	67
3.2 Protonation and Complex Formation Equilibria of Glycine and α-Alanine	68
3.2.1 Glycine	68
3.2.1.1 Titration Curves for Glycine and its Complexes	68
3.2.1.2 Protonation Constants of Glycine	80
3.2.1.3 Distribution Diagram for Glycine	82
3.2.1.4 Stability Constants of the Metal(II) Ion-Glycine Complexes	82
3.2.1.5 Distribution Diagrams for the Metal(II) Ion-Glycine Complexes	99
3.2.2 α -Alanine	111
3.2.2.1 Titration Curves for α -Alanine and its Metal(II) Ion Complexes	111

3.2.2.2 Protonation Constants of α -Alanine	111
3.2.2.3 Stability Constants of the Metal(II) Ion- α -Alanine Complexes	118
3.2.2.4 Distribution Diagrams for the Metal(II) Ion α -Alanine Systems	124
3.2.3 Ternary Complexes of Glycine, α -Alanine and Divalent Metal Ions	131
3.2.3.1 Titration Curves for the Ternary Complexes	131
3.2.3.2 Stability Constants of the Mixed Ligand Complexes	136
3.2.3.3 Distribution Diagrams for the Mixed Ligand Complexes	139
3.3 Concluding Comments	144

References

Appendix

Arabic Summary

Acknowledgment

I express my heartfelt gratitude and appreciation to Prof.Dr. M.M. Osman, Professor of Analytical Chemistry and Dr. N.J. Lees-Gayed, Lecturer of Analytical and Inorganic Chemistry for their close supervision of this thesis and their valuable advice.

I also express my sincere thanks and appreciation to Prof.Dr. M.F. Iskander, Professor of Inorganic Chemistry and Prof.Dr. H.I. Emara, Professor of Marine Chemistry for their encouragement and continuous help.

I am deeply indebted to Dr. S.A. Kholeif, Lecturer in Analytical Chemistry for supplying me the SUPERQUAD and WSTD programs, performing some of the computation, valuable discussion and continuous help.

Thanks and appreciation are also given to the Dean of Faculty of Science for his continuous help and support.

My sincere gratitude is extended to the Chemistry Department, Faculty of Science for supporting me with all material facilities.

Abbreviations

asv	anodic stripping voltammetry
HL	glycine
HL'	α -alanine
NBS	National Bureau of Standard, Washington, D.C., U.S.A.
NPL	National Physical Laboratory, Teddington, U.K.

SUMMARY

Summary

This thesis is concerned with the acid-base equilibria of the amino acids glycine and α -alanine, as well as the complex formation equilibria of glycine with the divalent metal cations magnesium(II), calcium(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II), and of α -alanine with cobalt(II), nickel(II), copper(II) and zinc(II).

The formation equilibria of the ternary complexes of glycine, α -alanine and each of the cobalt(II), nickel(II), copper(II) and zinc(II) ions are also considered. The medium used was an artificial seawater (of ionic strength $0.701 \text{ mol dm}^{-3}$), at temperature of $25.0 \pm 0.1^\circ\text{C}$. Investigation of the selfionization equilibrium of water and the protonation equilibrium of the sulphate ion under the same conditions is also described in this thesis.

The thesis is divided into three chapters.

The first is an introductory chapter which explains the importance of equilibrium data valid for media approximating natural aquatic systems, and also briefly describes the various methods used to investigate speciation in aquatic environments. The literature on the protonation of glycine and α -alanine, their complex formation with the metals considered in this thesis, in natural seawater, artificial seawater and in media of ionic strength around 0.7 mol dm^{-3} , is surveyed.