A POLAROGRAPHIC AND POTENTIOMETRIC STUDY OF METAL – LIGAND EQUILIBRIA: INSTRUMENTATION AND INVESTIGATIONS OF SYSTEMS WITH NON – REVERSIBLE ELECTRODE REACTIONS

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DECLARATION

I declare that this dissertation is my own work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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(Signature of candidate)

_____ day of_____ 2006.

OUTPUTS FROM THIS WORK

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ABSTRACT

New possibilities in collection of polarographic and potentiometric experimental data in studies of metal–ligand systems by automated instrumental methods, and subsequent treatment of the polarographic data, whereby the degree of reversibility of the electrode processes varies, have been investigated in this work. An automated instrumental set–up was developed for applications in studies of metal–ligand solution equilibria by potentiometry and sampled Direct Current Polarography (DCP). The new set–up was designed based on virtual instrumentation principles whereby several commercially–available hardware units as well as custom–built electronic components, were interfaced to a personal computer that was equipped with appropriate hardware and control programs. The instrumental set–up was tested and validated by studying the protonation equilibria of the ligand glycine by Glass Electrode Potentiometry (GEP) as well as the complexation of the ligand glycine with Cd^{2+} by GEP and DCP. The new set–up provides increased versatility, accuracy and convenience in obtaining large numbers of experimental points in solution equilibria studies by DCP and GEP as opposed to the use of tedious and time–consuming manual methods. Nonlinear curve–fitting procedures, based on closed–form models that were derived here from suitable theoretical equations identified from literature, have been investigated in this work for applications in analysis of DC curves recorded on metal–ligand systems with variation in electrochemical reversibility. The applicability and limitations of the curve–fitting procedures developed have been tested in analysis of the DCP data collected on several metal–ligand systems involving Cd^{2+}, Pb^{2+}, Zn^{2+} and the ligands glycine and sarcosine, whereby the DCP studies of these systems exhibited reversible, quasi–reversible or irreversible electrochemical processes. Information on applicability and limitations of the proposed methods investigated in this work was derived by comparison of the results obtained from DCP, using the proposed methods, with either reported literature data and/or results obtained in this work by the independent analytical technique of GEP, which was deployed wherever it was found to be applicable to study the metal–ligand systems considered.

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TABLE OF CONTENTS

DECLARATION ii
OUTPUTS FROM THIS WORK iii
ABSTRACT iv
ACKNOWLEDGEMENTS v
LIST OF FIGURES x
LIST OF TABLES xxii
LIST OF ABBREVIATIONS xxvi

CHAPTER 1 INTRODUCTION

1.1 METAL–LIGAND EQUILIBRIA: GENERAL BACKGROUND 1
1.2 GENERAL CONCEPTS IN EQUILIBRIUM ANALYSIS 3
1.3 EXPERIMENTAL TECHNIQUES FOR METAL–LIGAND EQUILIBRIA STUDIES 7
1.3.1 General Survey 7
1.4 POTENTIOMETRY 9
1.4.1 Basic Principles of Potentiometry 9
1.4.2 Potentiometry and the Study of Metal–Ligand Equilibria 11
1.4.3 Computer–Assisted Experiments for Potentiometry 12
1.5 POLAROGRAPHY 15
1.5.1 Basic Principles of Polarography 15
1.5.2 Polarography and the Study of Metal–Ligand Equilibria 20
1.5.3 Reversibility of Electrode Reactions 25
1.5.4 Computer–Assisted Experiments for Polarography 29
1.6 AIMS AND SCOPE OF PROJECT 32
1.7 SUMMARY OF CHAPTERS 34
1.8 REFERENCES 36

CHAPTER 2 MATERIALS AND GENERAL EXPERIMENTAL PROCEDURES

2.1 REAGENTS 41
2.2 PREPARATION AND STANDARDISATION OF SOLUTIONS 42

2.3 GLASS ELECTRODE POTENTIOMETRY 43
2.3.1 Electrodes and Instrumentation..... 43
2.3.2 Experimental Set–up..... 44
2.3.3 Glass Electrode Calibration 44
2.3.4 Determination of Ligand Protonation Constants 46
2.3.5 Metal–Ligand Equilibria Studies by GEP..... 48
2.4 SAMPLED DIRECT CURRENT POLAROGRAPHY..... 49
2.4.1 Electrodes and Instrumentation..... 49
2.4.2 Experimental Set–up..... 51
2.4.3 Polarographic Studies of Metal–Ligand Equilibria 52
2.5 REFERENCES..... 55

CHAPTER 3 THEORY AND TREATMENT OF DATA

3.1 INTRODUCTION 56
3.2 GLASS ELECTRODE POTENTIOMETRY: THEORY, MODELLING AND REFINEMENT OF PROTONATION AND STABILITY CONSTANTS..... 56
3.3 SAMPLED DIRECT CURRENT POLAROGRAPHY: THEORY, MODELLING AND REFINEMENT OF STABILITY CONSTANTS..... 61
3.3.1 Optimisation of a Metal–Ligand Model and Refinement of Stability Constants..... 61
3.3.2 General Concepts in Modelling of Polarographic Data..... 64
3.3.2.1 Variation in Half–wave Potential as a Function of pH..... 64
3.3.2.2 Variation in Half–wave Potential versus Free Ligand Concentration 67
3.3.2.3 Variation in Limiting Diffusion Current as a Function of pH..... 68
3.4 VIRTUAL POTENTIOMETRY..... 68
3.5 ANALYSIS OF DIRECT CURRENT POLAROGRAMS RECORDED ON METAL–LIGAND SYSTEMS 70
3.5.1 Electrochemical Reversibility: General Concepts 70
3.5.2 Evaluation of Electrochemical Reversibility 75

3.5.2.1 Logarithmic Analysis 75
3.5.2.2 Curve–fitting Method 80
3.5.3 Determination of Reversible Half-wave Potential and Limiting Diffusion Current 83
3.5.3.1 Reversible or Nearly Reversible Systems 83
3.5.3.2 Non–reversible Systems 84
3.5.4 Concluding Remarks 91
3.6 REFERENCES 92

CHAPTER 4 DEVELOPMENT OF AUTOMATED INSTRUMENTATION

4.1 INTRODUCTION 95
4.1.1 General Concepts on Virtual Instrumentation 96
4.2 DESCRIPTION OF THE HARDWARE 98
4.2.1 Data Collection and Processing Interface 101
4.2.2 Electronic Control Box 102
4.2.3 Digital pH Meter 103
4.2.4 Digital Burette 103
4.2.5 Magnetic Stirrer 104
4.2.6 Potentiostat and Current–Measuring System 105
4.2.7 Voltammetric Stand 110
4.3 DESCRIPTION OF THE SOFTWARE 113
4.3.1 Potentiometry 113
4.3.2 Sampled Direct Current Polarography 119
4.3.3 Sampled Direct Current Polarography with Potentiometry 123
4.4 VALIDATION AND PERFORMANCE OF INSTRUMENTATION 133
4.4.1 Glass Electrode Potentiometry: Automated Titrations 133
4.4.1.1 Protonation Equilibria for Glycine 133
4.4.1.2 A Potentiometric Study of a Cadmium(II)–Glycine–OH system 137
4.4.2 Sampled Direct Current Polarography with Potentiometry: Automated Titrations 142
4.4.2.2 A Polarographic Study of a Cadmium(II)–Glycine–OH System 142

4.5 CONCLUSIONS 150
4.6 REFERENCES 151

CHAPTER 5 METAL–LIGAND SYSTEMS INVOLVING POLAROGRAPHIC REVERSIBLE AND NON–REVERSIBLE ELECTRODE REACTIONS

5.1 INTRODUCTION 153
5.2 RESULTS AND DISCUSSION 159
5.2.1 Case Study 1: A Cadmium(II)–Sarcosine–OH System 159
5.2.1.1 A GEP Study of a Cd(II)–Sarcosine–OH System 160
5.2.1.2 Polarographic Investigations of a Cd(II)–Sarcosine–OH System 166
5.2.2 Case Study 2: A Lead(II)–Glycine–OH System 186
5.2.3 Case Study 3: A Lead(II)–Sarcosine–OH System 200
5.2.4 Case Study 4: A Zinc(II)–Glycine–OH System 209
5.2.4.1 A GEP Study of a Zn(II)–Glycine–OH System 210
5.2.4.2 Polarographic Investigations of a Zn(II)–Glycine–OH System 215
5.2.5 The Effect of Addition of a Methyl Group to a Ligand 227
5.3 CONCLUSIONS 231
5.3.1 Applicability and Limitations of Curve–Fitting Models for Analysis of DC Polarograms 231
5.3.2 Recommended Procedures in Analysis of DC Polarograms Recorded On Metal–Ligand Systems 234
5.4 REFERENCES 237

CHAPTER 6 GENERAL CONCLUSIONS 239

APPENDICES 245

LIST OF FIGURES

Figure 1.1: An overall scheme for equilibrium model determination.....6

Figure 1.2: Sampled DC polarography. (a) Stepwise potential waveform. (b) Current–time curves observed in response to the potential steps and current sampling scheme 19

Figure 1.3: A typical sigmoidal–shaped sampled DC polarogram. 19

Figure 1.4: A flowchart depicting experimental tasks typically performed in a polarographic study of a metal–ligand system at fixed L_T : M_T and variable pH.. 31

Figure 2.1: An example of a calibration curve obtained prior to performing a glass electrode potentiometric experiment for a metal–ligand system.....46

Figure 2.2: A photograph showing electrodes and probes used in studies of metal–ligand systems at fixed L_T : M_T and variable pH 50

Figure 2.3: A photograph of the instrumental set–up in a typical automated experiment for a metal – ligand system at fixed L_T:M_T ratio and variable pH by sampled direct current polarography with glass electrode potentiometry as the leading technique.....51

Figure 3.1: A typical relationship of variation in half–wave potential for Cd^{2+}, in the presence of the protic ligand glycine, as a function of pH.....65

Figure 3.2: An example of a typical relationship of variation in half–wave potential as a function of Log [L].....67

Figure 3.3: Schematic comparison of DC polarograms corresponding to reversible, quasi–reversible, and irreversible reduction processes 73

Figure 3.4: A sampled direct current polarogram for the reversible reduction of Pb^{2+} 25 °C in 0.5 M $NaNO_3$ 78

Figure 3.5: A logarithmic analysis corresponding to the DC polarogram for the reversible reduction of Pb^{2+} at 25 °C in 0.5 M $NaNO_3$ shown in Figure 3.4 78

Figure 3.6: A sampled direct current polarogram for a quasi–reversible reduction of Cd^{2+} at 25 °C in 0.5 M $NaNO_3$ in the presence of the ligand sarcosine 79

Figure 3.7: A logarithmic analysis of the DC polarogram in Figure 3.6 80

Figure 3.8: An example of the analysis of a quasi–reversible DC polarogram for the reduction of Cd^{2+} at 25 °C in 0.5 M $NaNO_3$, in the presence of the ligand sarcosine, using the Cukrowski's curve–fitting method 85

Figure 3.9: Logarithmic analysis of a quasi–reversible DC polarographic wave using the Matsuda–Ayabe method 88

Figure 4.1: A block diagram showing interfacing and connectivity of the various hardware components of the instrumental set–up for potentiometric and polarographic measurements 99

Figure 4.2: A simplified circuit diagram showing connectivity and interfacing of the electronic components used in the instrumentation for automated DC polarographic and potentiometric measurements 100

Figure 4.3: A basic potentiostatic three–electrode system with measurement of cell current via a current–to–voltage converter.....106

Figure 4.4: The integration amplifier circuitry used for amplification of the current response signals measured by the CV–27 voltammograph.....107

Figure 4.5: A schematic diagram showing the inert gas connections and operating principle of the valve block and multi–mode electrode of the 663 VA stand.....111

Figure 4.6: A flow chart of the *Configure Dosimat & pH meter VI* (the virtual instrument used to configure the pH meter and the digital burette (765 Dosimat) used in automated potentiometric–polarographic experiments).....114

Figure 4.7: The front panel of the *Autotitrator VI*, the software module developed for automated potentiometric titrations with constant volume additions 115

Figure 4.8: Flow chart of the *Autotitrator VI*, the virtual instrument for automated potentiometric titrations with constant volume additions 116

Figure 4.9: A flowchart of the subroutine (or SubVI) *Sampling 713/780 pH Meter* used to programmatically establish an equilibrium potential reading, at a particular titration stage, during an automated potentiometric titration.....118

Figure 4.10: The front panel (user–interface) of the *DC* (*One Polarogram*) *VI* used for single Sampled Direct Current Polarographic scans.....121

Figure 4.11: A flowchart of the *DC* (*One Polarogram*) *VI* used to generate single scans of Sampled DC polarography.....122

Figure 4.12: The front panel of the *AUTOTITRATOR-DC1 VI*, a software module used for automated titrations with acquisition of sampled DC polarograms and potentiometric data.....124

Figure 4.13: An example of a titration curve (pH versus volume of titrant) obtained from a study of Cd(II)–Glycine–OH system at fixed L_T: M_T ratio and variable pH 125

Figure 4.14: A flowchart showing programmatic execution of the *Autotitrator-DC1 VI* 126

Figure 4.15: Examples of recorded Sampled DC polarograms using the *Autotitrator-DC2 VI* used in an automated potentiometric–polarographic experiment of Pb(II)–Glycine–OH system at a fixed L_T:M_T ratio and variable pH.....129

Figure 4.16: The front panel of the *AUTOTITRATOR-DC-DYNAMIC2 VI* 130

Figure 4.17: A flowchart showing the programmatic execution of the VI *Autotitrator-DC-Dynamic2* 131

Figure 4.18: The chemical structure of a fully–protonated glycine molecule 133

Figure 4.19: A titration curve obtained from the titration of a glycine solution with 0.05 M NaOH 135

Figure 4.20: Experimental (o) and theoretical (solid line) protonation curves of the ligand glycine obtained from refinement of the GEP data collected using the automated instrumental set–up for potentiometric titrations developed in this project 137

Figure 4.21: Experimental (o) and theoretical (solid line) potentiometric complex formation curves obtained for the metal–ligand models containing ML, ML_2, ML_3, ML(OH), and $ML_2(OH)$ with the optimized stability constants for these complexes obtained from the study of Cd(II)–Glycine–OH system by GEP at various $L_T : M_T$ ratios.....140

Figure 4.22: A species distribution diagram for the Cd(II)–Glycine–OH system at $L_T : M_T = 1 : 1$, $[M_T] = 7.771 \times 10^{-3}$ M generated using the model containing M(HL), ML, ML_2, ML_3, ML(OH) and $ML_2(OH)$.....141

Figure 4.23: A species distribution diagram for the Cd(II)–Glycine–OH system at $L_T : M_T = 3 : 1$, $[M_T] = 4.679 \times 10^{-3}$ M generated using stability constants from the model containing M(HL), ML, ML_2, ML_3, ML(OH), $ML_2(OH)$.....142

Figure 4.24: Examples of sampled DC curves recorded during a study of Cd(II)–Glycine–OH ($L_T : M_T = 200 : 1$(fixed) and variable pH; $[M_T] = 1.016 \times 10^{-4}$ M). An illustration of the curve–fitting operations is also shown.....144

Figure 4.25: An example of interpretation of the observed shift in half–wave potential plotted against pH for the Cd(II)–Glycine–OH system studied by sampled DCP at experimental conditions as indicated for Figure 4.24 145

Figure 4.26: An example of interpretation of the observed shift in half–wave potential plotted against Log [L] for the Cd(II)–Glycine–OH system studied by DCP at fixed $L_T : M_T$ ratio and variable pH at experimental conditions as indicated for Figure 4.24.....146

Figure 4.27: Experimental (circles) and calculated (solid line) complex formation curves obtained for the Cd(II)–Glycine–OH system studied at a fixed $L_T : M_T$ ratio of 700; $[M_T] = 8.456 \times 10^{-5}$ M.....146

Figure 4.28: Species distribution as a function of pH for the Cd(II)–Glycine–OH system at $L_T : M_T = 200$; $[M_T] = 1.016 \times 10^{-4}$ M.....147

Figure 4.29: Species distribution as a function of pH for the Cd(II)–Glycine–OH system at $L_T : M_T = 600$; $[M_T] = 8.051 \times 10^{-5}$ M.....149

Figure 5.1: Chemical structures of the fully–protonated forms of the ligands Glycine, Sarcosine, Iminodiacetic acid (IDA) and *N*–methyliminodiacetic acid (MIDA) 157

Figure 5.2: A plot of variation in Log β_{ML} values plotted as a function of the metal ion radius for the metal ions Ni(II), Zn(II), Cu(II), Cd(II), and Pb(II) with the ligands iminodiacetic acid (IDA) and *N*–methyliminodiacetic acid (MIDA) at ionic strength of 0.5 M and 25 °C 157

Figure 5.3: A plot of variation in Log β_{ML} values plotted as a function of the metal ion radius for the metal ions Ni(II), Zn(II), Cu(II), Cd(II), and Pb(II) with the ligands Glycine and Sarcosine (*N*–methylglycine) at ionic strength of 0.5 M 158

Figure 5.4: Experimental (circles) and calculated (solid line) potentiometric complex formation curves for Cd(II)–Sarcosine–OH system at $L_T : M_T = 2$, initial $[M_T] = 4.797 \times 10^{-3}$ M and $L_T : M_T = 7$, initial $[M_T] = 2.041 \times 10^{-3}$ M at 25 °C and ionic strength 0.5 M in $NaNO_3$.....162

Figure 5.5: Species distribution as a function of pH for the Cd(II)–Sarcosine–OH system at $L_T : M_T = 2$; $[M_T] = 4.797 \times 10^{-3}$ M 163

Figure 5.6: Species distribution as a function of pH for the Cd(II)–Sarcosine–OH system at $L_T : M_T = 7$; $[M_T] = 2.041 \times 10^{-3}$ M 164

Figure 5.7: Variation in the reversibility index parameter δ as a function of pH obtained from curve–fitting operations performed on the DC polarograms collected on a polarographic study of Cd(II)–Sarcosine–OH system at $L_T : M_T = 98$, ionic strength = 0.5 M, 25 °C , $[M_T] = 2.035 \times 10^{-4}$ M.....167

Figure 5.8: Examples of analyses of DC polarograms by nonlinear curve–fitting operations to estimate I_d and $E^r_{1/2}$ 169

Figure 5.9: Comparison of the observed $E_{1/2}$ values (uncorrected for departure from electrochemical reversibility) and reversible half–wave potentials ($E^r_{1/2}$) obtained using different nonlinear curve–fitting models.....171

Figure 5.10: Variation in limiting diffusion current for Cd(II)–Sarcosine–OH system studied by sampled DC polarography at $L_T : M_T$ ratio 98, at $L_T : M_T = 98$, ionic strength = 0.5 M, 25 °C , initial $[M_T] = 2.035 \times 10^{-4}$ M.....173

Figure 5.11: Prediction of major metal containing species from analysis of variation in half–wave potentials as a function of pH.....174

Figure 5.12: Prediction of major metal containing species from analysis of variation in half–wave potentials as a function of free ligand concentration (expressed as Log [L]) 176

Figure 5.13: Experimental and calculated complex formation curves obtained using reversible half–wave potentials for the Cd(II)–Sarcosine–OH system studied by sampled DC polarography at $L_T : M_T = 98$, ionic strength = 0.5 M, 25 °C , initial $[M_T] = 2.035 \times 10^{-4}$ M. For comparison, the ECFC from observed half–wave potentials uncorrected for departure from electrochemical reversibility is also shown.....178

Figure 5.14: Species distribution as a function of pH for the Cd(II)–Sarcosine–OH system at $L_T : M_T = 98$; $[M_T] = 2.035 \times 10^{-4}$ M 181

Figure 5.15: Species distribution as a function of pH for the Cd(II)–Sarcosine–OH system at $L_T : M_T = 7$; $[M_T] = 2.041 \times 10^{-3}$ M (GEP conditions) 182

Figure 5.16: Virtual half–wave potential as a function of Log [M] computed with the use of the refined stability constants from the optimised model containing ML, ML_2, ML_3 for the Cd(II)–Sarcosine–OH system studied by sampled DC polarography at $L_T : M_T = 98$, ionic strength = 0.5 M, 25 °C , initial $[M_T] = 2.035 \times 10^{-4}$ M.....184

Figure 5.17: Comparison of the observed $E_{1/2}$ obtained using the Cukrowski curve–fitting method and $E^r_{1/2}$ obtained using the Ružić-based curve-fitting. The variation in the reversibility index parameter δ as a function of pH (obtained from the Cukrowski curve–fitting method) is also shown. DC polarograms collected on a polarographic study of Pb(II)–Glycine–OH system at $L_T : M_T = 800$, ionic strength = 0.5 M, initial $[M_T] = 8 \times 10^{-5}$ M 188

Figure 5.18: Variation in current as a function of pH for Pb(II)–Glycine–OH system studied by sampled DC polarography at L_T: M_T ratio 800, initial $[M_T] = 8 \times 10^{-5}$ M, ionic strength = 0.5 M and 25 °C 189

Figure 5.19: Prediction of major metal containing species from analysis of variation in virtual half–wave potentials as a function of pH for Pb(II)–Glycine–OH system studied by sampled DC polarography at L_T: M_T ratio 800, initial $[M_T] = 8 \times 10^{-5}$ M, 25 °C and ionic strength = 0.5 M 191

Figure 5.20: Prediction of major metal containing species from analysis of variation in virtual half–wave potentials as a function of Log [L] for Pb(II)–Glycine–OH system studied by sampled DC polarography at L_T: M_T ratio 800, initial $[M_T] = 8 \times 10^{-5}$ M, ionic strength = 0.5 M and 25 °C 192

Figure 5.21: Experimental and calculated complex formation curves for the Pb(II)–Glycine–OH system studied by sampled DC polarography at fixed L_T : M_T ratios, ionic strength of 0.5 M and 25 °C 193

Figure 5.22: Species distribution as a function of pH for the Pb(II)–Glycine–OH system at L_T : M_T = 800; $[M_T] = 8 \times 10^{-5}$ M.....195

Figure 5.23: Species distribution as a function of pH for the Pb(II)–Glycine–OH system at L_T : M_T = 800; $[M_T] = 8 \times 10^{-5}$ M.....196

Figure 5.24: Species distribution as a function of pH for the Pb(II)–Glycine–OH system generated for L_T : M_T = 800 and $[M_T] = 8 \times 10^{-5}$ M (conditions employed in this work) using the stability constants from literature [3] for the model with M(HL), $M(HL)_2$, $M(HL)_3$, ML, and ML_2 together with all known stability constants for $Pb_x(OH)_y$ complexes 197

Figure 5.25: Virtual half–wave potential as a function of Log [M] computed with the use of the refined stability constants from the optimised model containing M(HL), ML, ML_2, ML_3 for the Pb(II)–Glycine–OH studied by sampled DC polarography at L_T : M_T = 600, ionic strength = 0.5 M, 25 °C , initial $[M_T] = 8.062 \times 10^{-5}$ M.....198

Figure 5.26: Examples of analyses of DC polarograms from a sampled DC polarographic study of Pb(II)–Sarcosine–OH system at L_T : M_T = 400, μ = 0.5 M, 25 °C , $[M_T] = 7.990 \times 10^{-5}$ M.....202

Figure 5.27: Variation in reversible and observed half–wave potentials (uncorrected for departure from electrochemical reversibility) as a function of pH for the Pb(II)–Sarcosine–OH system at $L_T : M_T = 400$, $[M_T] = 7.990 \times 10^{-5}$ M, 25 °C , $\mu = 0.5$ M.....203

Figure 5.28: Variation in limiting diffusion current I_d as a function of pH for the Pb(II)–Sarcosine–OH system studied by sampled DC polarography at $L_T : M_T = 400$, $[M_T] = 7.990 \times 10^{-5}$ M, 25 °C , $\mu = 0.5$ M 204

Figure 5.29: Variation in virtual half–wave potential as a function of pH for the Pb(II)–Sarcosine–OH system 205

Figure 5.30: Variation in virtual half–wave potential as a function of free ligand concentration (expressed as Log[L]) for the Pb(II)–Sarcosine–OH system 206

Figure 5.31: Species distribution as a function of pH for the Pb(II)–Sarcosine–OH system generated for $L_T : M_T = 400$ and $[M_T] = 8 \times 10^{-5}$ M (conditions employed in this work) using the stability constants for the model containing M(HL), ML, ML_2, ML_3, and $ML_2(OH)_2$, together with all known stability constants for $Pb_x(OH)_y$ complexes 208

Figure 5.32: Experimental (circles) and theoretical (solid line) potentiometric complex formation curves obtained for the study of Zn(II)–Glycine–OH system by GEP at $L_T : M_T$ ratio 6, $[M_T] = 1.096 \times 10^{-3}$ M, 25 °C , and $\mu = 0.5$ M.....213

Figure 5.33: Species distribution as a function of pH for the Zn(II)–Glycine–OH system at $L_T : M_T$ ratio 1 : 1, $[M_T] = 9.838 \times 10^{-3}$ M 214

Figure 5.34: Species distribution as a function of pH for the Zn(II)–Glycine–OH system at $L_T : M_T$ ratio 6 : 1, $[M_T] = 1.096 \times 10^{-3}$ M 214

Figure 5.35: Typical polarograms of Zn(II) at various pH values recorded in a sampled DC polarographic study of Zn(II)–Glycine–OH system 216

Figure 5.36: A species distribution diagram for the Zn(II)–Glycine–OH system generated for the experimental conditions employed in the DC polarographic study of the system ($L_T : M_T = 240 : 1$, $[M_T] = 1.07 \times 10^{-4}$ M) 217

Figure 5.37: An example of analysis of a quasi–reversible DC polarogram from a DCP study of a Zn(II)–Glycine–OH system below pH 6 at $L_T : M_T = 240$, 25 °C , $\mu = 0.5$ M, initial $[M_T]=1.07 \times 10^{-4}$ M 219

Figure 5.38: An example of analysis of DC polarograms by nonlinear curve–fitting using the curve–fitting method based on the Ružić equation (Equation 3.49) for polarograms collected above pH 9 from a DCP study of a Zn(II)–Glycine–OH system. $L_T : M_T =$ 240, initial $[M_T] = 1.07 \times 10^{-4}$ M 220

Figure 5.39: A logarithmic analysis performed on the DC polarogram shown in Figure 5.38. The linearity and the slope confirmed full irreversible nature of the polarogram 221

Figure 5.40: An example of analysis of two overlapping DC waves from the polarographic study of a Zn(II)–Glycine–OH system and their resolution by curve–fitting. $L_T : M_T = 240$, initial $[M_T] = 1.07 \times 10^{-4}$ M, curve recorded at pH 7.091 223

Figure 5.41: Polarographic complex formation curves for the Zn(II)–Glycine–OH system at $L_T : M_T = 240$, initial $[M_T] = 1.04 \times 10^{-4}$ M, 25 °C and $\mu = 0.5$ M 225

Figure 5.42: Experimental (circles) and calculated (solid line) polarographic complex formation curves for the Zn(II)–Glycine–OH system from refinement of data in the pH range 5 to 7.5 226

Figure 5.43: Variation in Log β_{ML} values as a function of the metal ion radius for the metal ions Ni(II), Zn(II), Cu(II), Cd(II), and Pb(II) with the ligands Glycine and Sarcosine (*N*-methylglycine) at ionic strength of 0.5 M and 25 °C . Third order polynomial functions were found to be sufficient to generate the trend-lines shown 229

LIST OF TABLES

Table 1.1: A list of experimental methods available for investigations of metal–ligand equilibria 8

Table 4.1: Some specifications for the burette cylinders (exchange units) used with a 765 Dosimat (digital burette) 104

Table 4.2: A summary of the main features of the virtual instruments used for automated titrations with combined Sampled DCP and Potentiometric measurements on a sample solution 132

Table 4.3: (A) Dissociation constant for water (fixed in the refinement operations). (B) Summary of protonation constants for the ligand glycine obtained from refinement operations of GEP data collected using the automated potentiometric instrumental set–up developed in this project at 25 ℃ and ionic strength of 0.5 M in $NaNO_3$. (C) Summary of results from refinement operations that included refinement of initial acid concentrations 136

Table 4.4: (A) Protonation constants for the ligand glycine (L^-), dissociation constant for water and overall stability constants for Cd(II) complexes with OH^- included in the Cd(II)–L–OH model and used in the refinement procedures for GEP data. (B) Overall stability constants for Cd(II) with glycine from the literature and found in this work by GEP at 25 ℃ and ionic strength μ = 0.5 M ($NaNO_3$) 139

Table 4.5: (A) Protonation constants for the ligand glycine (L^-), dissociation constant for water and overall stability constants for Cd(II) complexes with OH^- included in the Cd(II)–L–OH model and used in the refinement procedures for Sampled DC polarographic data. (B) Overall stability constants for Cd(II) with glycine from the literature and found in this work by Sampled DC polarography at 25 ℃ and ionic strength of 0.5 M in $NaNO_3$ 148

Table 5.1: Summary of curve–fitting methods used in analysis of DC polarograms recorded on metal–ligand systems in order to estimate reversible half–wave potentials and limiting diffusion currents 155

Table 5.2: (A) Protonation constants for the ligand Sarcosine (L^-), dissociation constant for water and overall stability constants for Cd(II) complexes with OH^- included in the Cd(II)–L–OH model and used as fixed values in the refinement procedures of GEP data. (B) Overall stability constants for Cd(II) with sarcosine found in this work by GEP (at 25 ℃ and ionic strength μ = 0.5 M in $NaNO_3$) and those reported elsewhere 165

Table 5.3: (A) Overall stability constants for Cd(II)–Sarcosine–OH system found in this work by Sampled DC polarography using half–wave potential values from various curve–fitting models used in analysis of the DC polarograms. $L_T : M_T = 98$; initial $[M_T] = 2.035 \times 10^{-4}$ M, at 25 ℃ and ionic strength of 0.5 M in $NaNO_3$. (B) Overall stability constants for Cd(II)–Sarcosine–OH system found by GEP in this work and elsewhere 180

Table 5.4: Overall stability constants for Cd(II) with sarcosine found in this work by virtual potentiometry (VP) (generated from sampled DCP, $L_T : M_T$ ratio 98) and combined refinement operation of the VP and GEP data ($L_T : M_T$ ratios 2 and 7) 185

Table 5.5: (A) Protonation constants for the ligand Glycine (L^-), dissociation constant for water and overall stability constants for Pb(II) complexes with OH^- included in the Pb(II)–L–OH model and used in the refinement procedures of sampled DCP data. (B) Overall stability constants for Pb(II) with glycine found in this work by sampled DC polarography (at 25 ℃ and ionic strength μ = 0.5 M in $NaNO_3$) and those reported elsewhere 194

Table 5.6: Some overall stability constants for Pb(II) with glycine found in this work by virtual potentiometry (VP) (generated from sampled DCP, L_T : M_T ratio 600) 199

Table 5.7: (A) Protonation constants for the ligand Sarcosine (L^-), dissociation constant for water and overall stability constants for Pb(II) complexes with OH^- included in the Pb(II)–L–OH model and used in the refinement procedures of sampled DCP data. (B) Overall stability constants for Pb(II)–Sarcosine–OH system found in this work by Sampled DC Polarography at L_T : M_T = 400; initial $[M_T] = 7.990 \times 10^{-5}$ M, at 25 ℃ and μ = 0.5 M in $NaNO_3$ 207

Table 5.8: (A) Protonation constants for the ligand Glycine (L^-), dissociation constant for water and overall stability constants for Zn(II) complexes with OH^- included in the Zn(II)–L–OH model and used as fixed values in the refinement procedures of GEP data. (B) Overall stability constants for Zn(II) with glycine found in this work by GEP (at 25 ℃ and ionic strength, μ = 0.5 M in $NaNO_3$) and those reported elsewhere 212

Table 5.9: Overall stability constants for Zn(II)–Glycine–OH system found in this work by DCP, GEP and Virtual Potentiometry (VP) and those reported elsewhere. DCP data collected for L_T : M_T = 240; initial $[M_T] = 1.04 \times 10^{-4}$ M, at 25 ℃ and ionic strength of 0.5 M in $NaNO_3$ 228

Table 5.10 Stability constants (as Log β_{ML}) for complexes between glycine derivatives and some divalent metal ions. Stability constants are from [3] except for Cd(II)–Glycine, Cd(II)–Sarcosine, Pb(II)–Glycine and Pb(II)–Sarcosine [this work]. All values are at 25 °C and ionic strength = 0.5 M. 230

LIST OF ABBREVIATIONS

AC	Alternating Current
ADC	Analog–to–Digital Converter
AE	Auxiliary Electrode (Also referred to as counter electrode)
AI	Analog Input
AO	Analog Output
CCFC	Calculated Complex Formation Curve
CGE	Combination glass electrode
℃	Degrees Celsius
DAC	Digital–to–Analog Converter
DAQ card	Data Acquisition card
DC	Direct Current
DCP	Direct Current Polarography (Sampled Direct Current Polarography)
DME	Dropping Mercury Electrode
DO	Digital Output
$E^{r}_{1/2}$	Reversible half-wave potential of a DC polarogram
$E°$	Standard Potential
$E_{1/2}$	Half-wave potential as observed from a DC polarogram
E^{k}	Glass electrode constant from calibration
E_{appl}	Stepwise applied potential
ECFC	Experimental Complex Formation Curve
$E_{1/2}$(virt)	Virtual half–wave potential
emf	Electromotive force; potential
ESTA	Equilibrium Simulation for Titration Analysis; A suite of computer programs for analysis of potentiometric data.
Exp.	Experiment
F	Faraday Constant; 96485 C mol^{-1}
F.W.	Formula Weight of a compound
GEP	Glass Electrode Potentiometry
H	Proton; hydrogen ion; H^+
[i]	Molar concentration of species *i*
I–E	Refers to a plot of current (*I*) as a function of potential (*E*)
I_b	Background current corresponding to an electrochemical process at the dropping mercury electrode as obtained from a polarogram
I_d	Limiting diffusion current corresponding to an electrochemical process at the dropping mercury electrode as obtained from a polarogram
I_{obs}	Observed total current corresponding to an electrochemical process at the dropping mercury electrode as obtained from a polarogram
I_{red}	Reduction current corresponding to an electrochemical process at the dropping mercury electrode as obtained from a polarogram
K	Kelvin
KHP	Potassium Hydrogen Pthalate
K_w	Dissociation Constant for water; $K_w = [H^+][OH^-]$
L	Ligand (charge omitted for clarity)

L_T	Total ligand concentration in moles per Liter; $[L_T]$
$L_T : M_T$	Total ligand to total metal ion concentration ratio, i.e., $[L_T] / [M_T]$
M	As a symbol for metal ion (charge omitted for clarity) or as a unit for molar concentration, that is, number of moles of solute per 1 Liter of solution
MBE	Mass Balance Equation
MME	Multi–Mode Electrode
M_T	Total metal ion concentration in moles per Liter; $[M_T]$
mV	milliVolt = 1/1000 Volts
n	Number of electrons involved in an electrochemical reaction
NBAR	The average number of protons per ligand in the absence of metal ion
pA	–Log[L]; negative logarithm of the free deprotonated ligand concentration
PC	Personal Computer
pH	$-\text{Log}\,[H^+]$; Calculated pH using the calibration method involving strong acid/strong base titration at fixed ionic strength and temperature.
PTFE	Polytetrafluoroethylene
QBAR	Deprotonation function; the average number of protons released as a result of complexation per metal ion
R	Universal gas constant; 8.314 J mol^{-1} K^{-1}
RE	Reference Electrode
Refs.	References
s	Response slope for glass electrode
T	Temperature (in Kelvin)
T–Probe	Temperature Probe
VI	Virtual Instrument
VP	Virtual Potentiometry
WE	Working Electrode
ZBAR(H)	Potentiometric Complex Formation function; the average number of protons bound per ligand
ZBAR(M)	Potentiometric Complex Formation function; the average number of ligand molecules bound per metal ion
α	Cathodic transfer coefficient
β	Overall Stability Constant
δ	Electrochemical reversibility index or steepness coefficient parameter from analysis of direct current polarograms by a nonlinear curve–fitting procedure
μ	Ionic strength
3D–CFC	Three Dimensional Complex Formation Curves; A computer program for analysis of polarographic data for refinement of stability constants