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

Tumaini Samwel Peter Mkwizu

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, in fulfillment of the requirements for the degree of Master of Science

Johannesburg, 2006

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.

_____

(Signature of candidate)

_____ day of_____ 2006.

OUTPUTS FROM THIS WORK

Conference Papers:

Tumaini Mkwizu and Ignacy Cukrowski. Automated Instrumentation for Potentiometry and Polarography in Metal–Ligand Equilibria Studies, *Proceedings of the 37th National Convention of the South African Chemical Institute*, Pretoria July 2004.

Publications:

Ignacy Cukrowski, Tumaini S. Mkwizu, and Philemon Magampa. Voltammetry as Virtual Potentiometric Sensor in Modelling of a Metal/Ligand System and Refinement of Stability Constants. Part 5. Complexation Studies of Hydrolysis–Prone Lead(II) with Glycine and Sarcosine by Sampled–Direct–Current Polarography Involving Virtual Potential. (Manuscript submitted for publication in 2006).

Ignacy Cukrowski, Helder Marques, Tumaini S. Mkwizu, Philemon P. Magampa, and Claudette Serge. Influence of electronic and steric effects on stability constants and electrochemical reversibility of divalent ion complexes with glycine and sarcosine. A Glass Electrode Potentiometric, Sampled Direct Current Polarographic, Virtual Potentiometric, and Molecular Modelling study. (Manuscript in final preparation to be submitted for publication in 2006).

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.

ACKNOWLEDGEMENTS

First and foremost, I wish to express my most sincere gratitude to my research mentor Prof. Ignacy Cukrowski. I found great pleasure in working with and learning from him. I thank him for his patience, academic guidance, as well as moral and financial support which he provided me throughout the duration of the research project. My sincere appreciation also goes to Mr. Basil Chassoulas of the Wits School of Chemistry for his tremendous assistance in the electronic aspects related to the development of instrumentation in this project. Thank you, to all my colleagues at the Electrochemistry Research Laboratories (at Wits University and currently at the Department of Chemistry, University of Pretoria). Their contributions in many ways toward the success of this project are highly appreciated. I also wish to thank the University of the Witwatersrand for financial support through a Postgraduate Merit Award programme. My deep gratitude also goes to the staff of the School of Chemistry at Wits University for technical and administrative assistance they provided me during my studentship in the School. Finally, my deepest gratitude goes to my parents for their moral and financial support, offered to me wholeheartedly, during my tenure as a postgraduate student in the Republic of South Africa.

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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