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

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Science

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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.

_______________________________
(Signature of candidate)

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OUTPUTS FROM THIS WORK

Conference Papers:


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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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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>ADC</td>
<td>Analog–to–Digital Converter</td>
</tr>
<tr>
<td>AE</td>
<td>Auxiliary Electrode (Also referred to as counter electrode)</td>
</tr>
<tr>
<td>AI</td>
<td>Analog Input</td>
</tr>
<tr>
<td>AO</td>
<td>Analog Output</td>
</tr>
<tr>
<td>CCFC</td>
<td>Calculated Complex Formation Curve</td>
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<tr>
<td>CGE</td>
<td>Combination glass electrode</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>DAC</td>
<td>Digital–to–Analog Converter</td>
</tr>
<tr>
<td>DAQ card</td>
<td>Data Acquisition card</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DCP</td>
<td>Direct Current Polarography (Sampled Direct Current Polarography)</td>
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<tr>
<td>DME</td>
<td>Dropping Mercury Electrode</td>
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<td>DO</td>
<td>Digital Output</td>
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</tr>
<tr>
<td>E°</td>
<td>Standard Potential</td>
</tr>
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<tr>
<td>ECFC</td>
<td>Experimental Complex Formation Curve</td>
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<tr>
<td>E&lt;sub&gt;1/2 (virt)&lt;/sub&gt;</td>
<td>Virtual half–wave potential</td>
</tr>
<tr>
<td>emf</td>
<td>Electromotive force; potential</td>
</tr>
<tr>
<td>ESTA</td>
<td>Equilibrium Simulation for Titration Analysis; A suite of computer programs for analysis of potentiometric data.</td>
</tr>
<tr>
<td>Exp.</td>
<td>Experiment</td>
</tr>
<tr>
<td>F</td>
<td>Faraday Constant; 96485 C mol&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td>F.W.</td>
<td>Formula Weight of a compound</td>
</tr>
<tr>
<td>GEP</td>
<td>Glass Electrode Potentiometry</td>
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<tr>
<td>H</td>
<td>Proton; hydrogen ion; H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
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<td>I&lt;sub&gt;red&lt;/sub&gt;</td>
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<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>KHP</td>
<td>Potassium Hydrogen Pthalate</td>
</tr>
<tr>
<td>K&lt;sub&gt;w&lt;/sub&gt;</td>
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</tr>
<tr>
<td>L</td>
<td>Ligand (charge omitted for clarity)</td>
</tr>
</tbody>
</table>
L
\text{\textsubscript{T}} \quad \text{Total ligand concentration in moles per Liter; } [L\text{\textsubscript{T}}]

L
\text{\textsubscript{T}} : M
\text{\textsubscript{T}} \quad \text{Total ligand to total metal ion concentration ratio, i.e., } [L\text{\textsubscript{T}}] / [M\text{\textsubscript{T}}]

M \quad \text{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 \quad \text{Mass Balance Equation}

MME \quad \text{Multi–Mode Electrode}

M_T \quad \text{Total metal ion concentration in moles per Liter; } [M_T]

mV \quad \text{milliVolt } = \text{ } \frac{1}{1000} \text{ Volts}

n \quad \text{Number of electrons involved in an electrochemical reaction}

NBAR \quad \text{The average number of protons per ligand in the absence of metal ion}

pA \quad \text{–Log[L]; negative logarithm of the free deprotonated ligand concentration}

PC \quad \text{Personal Computer}

pH \quad \text{–Log } [H^+] ; \text{ Calculated pH using the calibration method involving strong acid/strong base titration at fixed ionic strength and temperature.}

PTFE \quad \text{Polytetrafluoroethylene}

QBAR \quad \text{Deprotonation function; the average number of protons released as a result of complexation per metal ion}

R \quad \text{Universal gas constant; } 8.314 \text{ J mol}^{-1} \text{ K}^{-1}

RE \quad \text{Reference Electrode}

Refs. \quad \text{References}

s \quad \text{Response slope for glass electrode}

T \quad \text{Temperature (in Kelvin)}

T–Probe \quad \text{Temperature Probe}

VI \quad \text{Virtual Instrument}

VP \quad \text{Virtual Potentiometry}

WE \quad \text{Working Electrode}

ZBAR(H) \quad \text{Potentiometric Complex Formation function; the average number of protons bound per ligand}

ZBAR(M) \quad \text{Potentiometric Complex Formation function; the average number of ligand molecules bound per metal ion}

\alpha \quad \text{Cathodic transfer coefficient}

\beta \quad \text{Overall Stability Constant}

\delta \quad \text{Electrochemical reversibility index or steepness coefficient parameter from analysis of direct current polarograms by a nonlinear curve–fitting procedure}

\mu \quad \text{Ionic strength}

3D–CFC \quad \text{Three Dimensional Complex Formation Curves; A computer program for analysis of polarographic data for refinement of stability constants}