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

5.1 INTRODUCTION

It must be noted that the development of an automated instrumentation for metal–ligand equilibria studies by polarography (as described in the preceding Chapter) allows for convenient and reliable way of acquiring large numbers of experimental points (DC polarograms) in a given experiment. Acquisition of large numbers of experimental points is a necessary but not a sufficient requirement for any useful analysis to be performed on a set of polarographic data, for which the final aim in the overall analysis is to arrive at a plausible metal–ligand model and computation of reliable stability constants. For a set of polarographic data to provide sufficient experimental information for use in rigorous analysis performed in modelling and refinement of stability constants, the polarograms recorded at various solution compositions have to be analysed as accurately as possible to provide (i) information on degree of electrochemical reversibility, as well as (ii) the necessary parameters \( I_d \) and \( E_{1/2} \) required in refinement operations for determination of stability constant.

As it was noted in the introductory chapter (section 1.5.3) and in Chapter 3 (section 3.5), the mathematical methods involved in the refinement of polarographic data require \( I_d \) and \( E_{1/2} \) resulting from reversible electrode processes that are due to reduction of at least one labile species in homogeneous equilibrium with other species in solution. It was also noted that most systems encountered in polarographic studies of metal–ligand systems involve non–reversible electrochemical processes that can be described as being quasi–reversible or irreversible depending on the extent of departure from reversibility. Consequently, recorded polarographic curves have to be analyzed as accurately as possible, (i) to establish electrochemical reversibility, and (ii) to obtain, if possible, the reversible
half-wave potential ($E_{1/2}$) and the $I_d$ values from the polarograms recorded at various solution composition.

In this chapter results and discussions related to application of the nonlinear curve–fitting models derived from literature and adopted in this work for analysis of DC polarograms (in estimation of $I_d$ and $E'_{1/2}$) are presented. The derivations and theoretical basis of the nonlinear curve–fitting models were described in section 3.5 of Chapter 3. For quick–reference purposes, a summary of the curve–fitting models is presented in Table 5.1.

Four metal–ligand systems were investigated by Sampled Direct Current Polarography at fixed $L_T : M_T$ ratios and variable pH. The metal–ligand systems are: Cd(II)–Sarcosine–OH, Pb(II)–Glycine–OH, Pb(II)–Sarcosine–OH, and Zn(II)–Glycine–OH. Applicability and limitations of the proposed nonlinear curve–fitting models in providing reliable $I_d$ and $E'_{1/2}$ (for use in determination of stability constants) were evaluated using the mentioned metal–ligand systems as case studies. Where possible, glass electrode potentiometric studies of the metal–ligand systems were also conducted as a means of testing and validating the applicability of the proposed methodologies for treatment of the polarographic data.

**Some background information on the metal–ligand systems studied**

Due to unavailability of automated instrumentation for acquisition of polarographic data in voltammetric studies of metal–ligand systems, a common practice was such that few experimental points were acquired in such studies. Large numbers of experimental points were not conveniently obtained by manual methods that were involved. Usually rough estimates of stability constants were obtained. Sometimes accurate values of stability constants are required, for instance, to explain some fundamental aspects such as structural changes on ligands and their effect on stability of complexes formed between the ligands and various metal ions [1].
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.

**Background Current:**

(i) For background current varying linearly with \( E_{\text{appl}} \): 
\[
I_b = a + bE_{\text{appl}}
\]

(ii) For background current initially varying linearly with \( E_{\text{appl}} \) and later varying exponentially with \( E_{\text{appl}} \) (e.g., \( \text{H}_2 \) evolution): 
\[
I_b = a + bE_{\text{appl}} + c \exp(-dE_{\text{appl}})
\]

**Cukrowski curve–fitting method**

Regression equation (Equation 3.33):
\[
I_{\text{obs}} = \frac{I_d}{\exp\left(\frac{\delta nF}{RT}(E_{\text{appl}} - E_{1/2}) + 1\right)} + I_b
\]

Regression parameters:
- \( I_d \), \( \delta \), \( E_{1/2} \), \( a \), \( b \) (Polarograms with linear background current)
- \( I_d \), \( \delta \), \( E_{1/2} \), \( a \), \( b \), \( c \), \( d \) (Polarograms with linear and exponential background currents)

**Method based on Matsuda–Ayabe equation**

Regression Equation (Equation 3.44):
\[
I_{\text{obs}} = \frac{I_d}{\Gamma \exp\left(\frac{\alpha nF}{RT}(E_{\text{appl}} - E_{1/2}) + \frac{\beta nF}{RT}(E_{\text{appl}} - E_{1/2}) + 1\right)} + I_b
\]

Regression parameters:
- \( I_d \), \( \alpha \), \( \beta \), \( E_{1/2} \), \( \Gamma \), \( a \), \( b \) (Polarograms with linear background current)
- \( I_d \), \( \alpha \), \( \beta \), \( E_{1/2} \), \( \Gamma \), \( a \), \( b \), \( c \), \( d \) (Polarograms with linear and exponential background currents)

**Method based on Ružić equation**

Regression equation (Equation 3.49):
\[
I_{\text{obs}} = \frac{I_d}{\exp\left(\frac{\alpha nF}{RT}(E_{\text{appl}} - E'_{1/2}) + \frac{\beta nF}{RT}(E_{\text{appl}} - E'_{1/2}) + 1\right)} + I_b
\]

Regression parameters:
- \( I_d \), \( \alpha \), \( \beta \), \( E'_{1/2} \), \( a \), \( b \) (Polarograms with linear background current)
- \( I_d \), \( \alpha \), \( \beta \), \( E'_{1/2} \), \( a \), \( b \), \( c \), \( d \) (Polarograms with linear and exponential background currents)
One such fundamental study was pursued in a preliminary investigation that was part of a Bachelor of Science (Honours) project [2]. In that project the complexation of the ligands glycine and sarcosine (N-methylglycine) with the metal ions Cd$^{2+}$ and Pb$^{2+}$ were studied in an attempt to elucidate the effect of addition of a methyl group to the nitrogen atom of the ligand glycine (effectively producing sarcosine) on complex stability involving various metal ions and the said ligands. Reliable stability constants in the literature were available for the Ni$^{2+}$, Zn$^{2+}$, and Cu$^{2+}$ [3]. With Cd(II)–Glycine–OH system reliable literature data were available, but the reported data for the Cd(II)–Sarcosine–OH system were regarded as uncertain when they were critically evaluated [3]. Moreover, for Pb(II)–Glycine–OH system the reported value for the ML complex was regarded to have some degree of uncertainty. No literature data was available in the case of Pb(II)–Sarcosine–OH system. The main reason for the difficulties encountered on studying the Pb(II) systems has been attributed to susceptibility of Pb$^{2+}$ to undergo hydrolysis, particularly when studied by potentiometry whereby the experimental conditions employed (low L$_T$ : M$_T$ ratios and large [M$_T$]) lead to precipitation [4]. Polarography was then seen as a useful alternative technique to study the Pb$^{2+}$ with glycine and sarcosine [2].

The typical trend observed for the addition of a methyl group to a donor atom of a ligand is that stability constants increase due to enhancement of the inductive effect provided by the added methyl group. A typical example is that between the ligands iminodiacetic acid (IDA) and N-methyliminodiacetic acid (MIDA). The chemical structures of the ligands glycine, sarcosine, IDA, and MIDA are shown in Figure 5.1. A trend of stability constants for the ML complex of various metal ions with IDA and MIDA, as a function of the metal ion radius of the metal ions involved, clearly shows that the methyl group addition to IDA (to form MIDA) leads to increase in stability constants (see Figure 5.2). The stability constants used in Figure 5.2 were compiled from literature [3]. Also, the metal ion radii used for the various metal ions were compiled from literature [5].
Figure 5.1: Chemical structures of the fully–protonated forms of the ligands Glycine, Sarcosine, Iminodiacetic acid (IDA) and $N$–methyliminodiacetic acid (MIDA).

Figure 5.2: A plot of variation in $\log \beta_{ML}$ 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.
Using stability constants data for the ML complex of Pb(II) and Cd(II) with the ligand sarcosine obtained from the preliminary study [2] and literature data for the other metal ions (Zn(II), Ni(II), Cu(II), and Cd(II)) with glycine and sarcosine [3], a plot of Log $\beta$ values for the ML complexes as a function of metal ion radius indicated that the addition of a methyl group to glycine (to produce sarcosine) leads to an opposite situation, whereby the stability constants for the sarcosine ML complexes are lower than those for the ML complexes of glycine (see Figure 5.3). However, due to the fact that the Log $\beta_{\text{ML}}$ values for Cd(II) and Pb(II) with sarcosine (obtained in the preliminary study [2]) when compared to those for glycine obtained elsewhere [3] appeared to be too close to each other ($\pm$ 0.1 Log units, this was within the experimental error of the data collected [2]). Thus, it could not be conclusively said that the trend observed was indeed the case.

**Figure 5.3:** A plot of variation in Log $\beta_{\text{ML}}$ 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. See text for details on the uncertainties involved for the case of Cd(II) and Pb(II).
Therefore, in this project the metal–ligand systems Cd(II)–Sarcosine–OH, Pb(II)–Glycine–OH, and Pb(II)–Sarcosine–OH were reinvestigated primarily for the following reasons: (i) to take advantage of the newly developed automated instrumentation (described in Chapter 4) in order to acquire a large set of experimental points. In the preliminary study [2], the titrations involved in the polarographic experiments performed were conducted manually and, as a result, few experimental points were acquired; (ii) to test usefulness of the proposed nonlinear curve–fitting models in analysis of DC polarograms in order to correct for the departure from electrochemical reversibility; (iii) to take advantage of the recent developments in the field of metal–ligand equilibria investigations by polarography. In particular, the recent methodology of Virtual Potentiometry (VP) (described in section 3.4 of Chapter 3) would be used, wherever it was found to be applicable, in modelling and refinement of stability constants.

In addition, the Zn(II)–Glycine–OH system was investigated because (i) there are reliable literature data obtained mainly from potentiometric studies [3–4]; and (ii) in polarographic studies of complexation of Zn(II) the electrochemical processes involved are generally non–reversible [6], hence the Zn(II)–Glycine–OH system was investigated as an additional case study for purposes of testing the applicability and limitations of the proposed methods for analysis of DC polarograms in estimation of $I_d$ and $E_{1/2}'$ for use in determination of stability constants.

5.2 RESULTS AND DISCUSSION

5.2.1 Case study 1: A Cadmium (II)–Sarcosine–OH system

Two experimental techniques, namely GEP and sampled DC polarography were used to investigate the solution equilibria of the Cd(II)–Sarcosine–OH system at several $L_T : M_T$ ratios and variable pH. An attempt to study the Cd(II)–Sarcosine–OH system by potentiometry was noted in the literature [6–7]. The reported data for the Cd(II)–
Sarcosine–OH system (reported in the 1950’s) did not meet the criteria for inclusion in the critically evaluated database of stability constants [3]. It was decided that before performing polarographic studies of the Cd(II)–Sarcosine–OH system, a reinvestigation of the system should be conducted firstly by GEP, taking advantage of the automated instrumentation for potentiometric titrations and modern software for evaluation of potentiometric data currently at our disposal. Furthermore, if GEP were to be found to provide reliable data, a direct comparison between polarographic results (the main focus in this project) and the GEP results would be made possible.

5.2.1.1 A GEP study of a Cd(II)–Sarcosine–OH system

In the GEP study of the Cd(II)–Sarcosine–OH system, two automated titrations were performed at \( L_T : M_T \) ratios 2 and 7 at fixed ionic strength of 0.5 M in NaNO\(_3\) aqueous medium at 25 °C. The GEP data were acquired between pH 2.5 and 8.7 (ratio 2) and pH 3 and 9.2 (ratio 7). To obtain the appropriate initial pH it was found necessary to add a known amount of standardised acid. Preliminary tests, that were done manually, indicated that precipitation occurs at about pH 9.5 for the experimental conditions employed for ratio 7 and at about pH 9 for the experimental conditions used in ratio 2.

The ESTA suite of programmes (described in section 3.2 of Chapter 3) was used for refinement operations to evaluate stability constants corresponding to plausible metal–ligand complexes. Experimental data for the Cd(II)–Sarcosine–OH system and outputs of refinement operations from ESTA have been documented in Appendix D. The data from the two titrations were initially refined independently and then combined and refined simultaneously to arrive to a reasonable final model.

In the refinement operations performed, different models containing the complexes M(HL), ML, ML\(_2\), ML\(_3\) and ML(OH) and ML\(_2\)(OH) were tested. The protonation constants for the ligand sarcosine, as well as all known stability constants for
Cd₃(OH)₂ complexes were kept constant during the refinement procedures. The
complex M(HL) was rejected in refinement operations when included in any model.
The preliminary polarographic study of Cd(II)–Sarcosine–OH system indicated
existence of M(HL) [2]. It seemed plausible to conclude that at the GEP experimental
conditions employed in this work (low Lₜ: Mₜ ratios), formation of the complex
M(HL) was negligible. Thus, this species was removed from further refinement
operations. Results from possible models considered are summarized in Table 5.2.
Since the ligand–metal sample solutions were acidified to attain suitable starting pH
in the titrations performed, the initial acid concentration was refined simultaneously
with the stability constants in all the refinement operations performed. The change in
the concentration of the acid was always less than ± 2 %, but the computed stability
constants were significantly improved as was suggested by the standard deviation and
Hamilton R-factor values.

In the refinement operations performed for the ratio 2 titration data, ESTA could
refined either a model with ML and ML₂ or ML and ML(OH). The overall statistical
parameter, the Hamilton R–factor, did not provide enough information on rejection or
acceptance of a particular model. ESTA could not simultaneously refine the stability
constants for the complexes ML₂ and ML(OH). This strongly indicated that the ESTA
program could not distinguish between ML₂ and MLOH it the solving mass–balance
equations. Species distribution diagrams generated using the experimental conditions
used for ratio 2 and the stability constants for the ML, ML₂ and MLOH showed that
formation of the species ML₂ and MLOH occurred in the same pH region where HL
is the major form of the ligand, and it involves the same amount of protons

\[ M^{2+} + 2HL \leftrightarrow ML₂ + 2H^+ \quad (5.1) \]

\[ M^{2+} + 2HL + H_2O \leftrightarrow ML(OH) + 2H^+ \quad (5.2) \]
Moreover, the computed stability constant value of 8.16 for ML(OH) was rather large compared to the expected theoretical value as predicted from hydrolysis of the ML complex (Log \( \beta_{ML} \) + Log \( \beta_{M(OH)} \) = 7.7).

![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 \texttimes 10^{-3} \text{ M} and L_T : M_T = 7, initial \([M_T]\) = 2.041 \texttimes 10^{-3} \text{ M} at 25 °C and ionic strength of 0.5 M in NaNO_3. The plots were generated using the model with ML, ML_2, and ML_3 using results in Table 5.2 from the combined refinement.]

Values of the complex formation function \( ZBAR(M) \), represented in Figure 5.4, were calculated for each datum point as described in Chapter 3 section 3.2. The \( ZBAR(M) \) functions strongly showed the formation of ML and ML_2 complexes with the \( ZBAR(M) \) values above 1 even for the ratio 2 titration data. No clear ‘backfanning’ feature was observable from the \( ZBAR(M) \) functions, but the function generated for the ratio 2 titration data showed a steep rise of the \( ZBAR(M) \) function above the values of 0.8 and toward the value of 1.2. The steep rise was suggestive of hydrolysis and that is why the complex ML(OH) was tried in optimisation of a plausible model.
In the refinement of ratio 7 titration data, ESTA could accept the model with ML, ML₂, ML(OH); ML, ML₂, ML₂(OH); or ML, ML₂, ML₃. ESTA could not simultaneously refine ML₃ together with neither ML(OH) nor ML₂(OH). Compared to ML and ML₂, larger standard deviations for the computed stability constants for MLOH, ML₂OH and ML₃ were observed. Species distribution diagrams generated using the refined stability constants for the different models always showed that the species MLOH, ML₂OH or ML₃ were always minor species compared to ML and ML₂. Since the ZBAR(M) functions did not indicate any significant hydrolysis and large standard deviations were obtained for the stability constants for the hydroxo complexes, refinement operations with the hydroxo species MLOH or ML₂(OH) were not considered as plausible.

**Figure 5.5:** Species distribution as a function of pH for the Cd(II)–Sarcosine–OH system at L₇: M₇ = 2; [M₇] = 4.797 × 10⁻³ M. The distribution was computed using results given in Table 5.2 using the model with ML, ML₂, and ML₃ together with all known Cdₓ(OH)ᵧ species from the combined refinement.

To arrive to the most plausible model from the GEP study of Cd(II)–Sarcosine–OH, the two potentiometric titration data were combined and refined by ESTA
simultaneously. The final model from the GEP data was tentatively taken with the model containing ML, ML$_2$, and ML$_3$, with reasonably accurate stability constants taken for the ML and ML$_2$ complexes.

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. The distribution was computed using results given in Table 5.2 using the model with ML, ML$_2$, and ML$_3$ together with all known Cd$_x$(OH)$_y$ species from the combined refinement.

Some species distribution diagrams for the Cd(II)–Sarcosine–OH system, generated using the stability constants for ML, ML$_2$, and ML$_3$ obtained from the final model in Table 5.2 and using conditions for $L_T$: $M_T$ ratios 2 and 7 are presented in Figures 5.5 and 5.6. Clearly, ML and ML$_2$ were the major species in the pH range were the actual experimental data were collected before precipitation occurred. Hence, the most accurate stability constant was obtained for the ML complex, followed by ML$_2$. 
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 °C and ionic strength, \( \mu = 0.5 \) M in NaNO3) and those reported elsewhere.

(A)

<table>
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<th>Equilibrium</th>
<th>Log ( \beta )</th>
<th>Equilibrium</th>
<th>Log ( \beta )</th>
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<td>( H^+ + OH^- \leftrightarrow H_2O )</td>
<td>13.74</td>
<td>( Cd^{2+} + OH^- \leftrightarrow Cd(OH)^+ )</td>
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<tr>
<td>( H^+ + L^- \leftrightarrow HL )</td>
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<td>( Cd^{2+} + 2OH^- \leftrightarrow Cd(OH)_2^+ )</td>
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<td>( HL + H^+ \leftrightarrow H_2L^+ )</td>
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<td>( Cd^{2+} + 3OH^- \leftrightarrow Cd(OH)_3^- )</td>
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<td></td>
<td></td>
<td>( Cd^{2+} + 4OH^- \leftrightarrow Cd(OH)_4^{2-} )</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>( 2Cd^{2+} + OH^- \leftrightarrow Cd_2(OH)_{3+} )</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 4Cd^{2+} + 4OH^- \leftrightarrow Cd_4(OH)_4^{2+} )</td>
<td>23.7</td>
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</table>

(B)

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<th>Log ( \beta )</th>
<th>Hamilton R–Factor</th>
<th>Remarks*</th>
<th>Refs.</th>
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<td>[M_HL]</td>
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<td>ML_2</td>
<td>ML_3</td>
<td>ML(OH)</td>
<td>[H^+] refined: 0.005923 ( \rightarrow 0.005427 ) M</td>
</tr>
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<td>2 : 1</td>
<td>4.797 \times 10^{-3}</td>
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<td>3.64 ± 0.02</td>
<td>7.07 ± 0.02</td>
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<td></td>
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<td>2.041 \times 10^{-3}</td>
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<td>3.85 ± 0.01</td>
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<td>7 : 1</td>
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* Final model from GEP in this work; [a] \( \mu = 0.5 \) M, 25 °C, Polarography; [b] Unspecified ionic strength, 25 °C, GEP
Species distribution diagram generated using experimental conditions for ratio 7, and using the results for the model containing ML, ML$_2$, and ML$_3$, clearly showed that ML$_3$ was a minor species, but not negligible species, at the pH where the experiment ended (maximum of about 9% at the pH where the experiment was ended). This would also explain why the refined stability constant for ML$_3$ was with high uncertainty. Most likely to obtain more accurate stability constant value for the ML$_3$ complex, data from higher L$_T$ : M$_T$ ratios would have to be considered. This was then left as an experimental task whereby polarography would be an advantageous technique.

5.2.1.2 Polarographic Investigations of a Cd(II)–Sarcosine–OH system

Sampled DC polarography was employed to study the Cd(II)–Sarcosine–OH system at fixed L$_T$ : M$_T$ ratio and variable pH at 25 °C and ionic strength of 0.5 M (in NaNO$_3$). Sampled DC polarograms were collected in the pH range 5 – 10.

(i) Analysis of DC polarograms and electrochemical reversibility

An initial step was the analysis of the DC polarograms collected, by way of nonlinear curve–fitting using the Cukrowski curve–fitting method (described in Chapter 3, section 3.5.2.2), to determine any variation in the degree of electrochemical reversibility in the pH range at which the polarograms were recorded. Figure 5.7 is a graphical representation of the variation in the reversibility index parameter $\delta$ (obtained from the curve–fitting operations performed on the DC polarograms) as a function of pH. For the curves in the pH range 5 to about pH 7.3, the reversibility index parameter $\delta$ varied from an initial value of 0.95 to 0.9 indicating that the electrochemical processes, which resulted in the DC polarograms obtained in this pH range, could be considered reversible.
Above pH 7.3, the parameter $\delta$ decreased steadily to a minimum value of about 0.6. The $\delta$ values below 0.9 indicated departure from electrochemical reversibility, i.e., quasi–reversible reduction processes occurred in the pH range 7.3 to 10. Therefore, in the case of Cd(II)–Sarcosine–OH system, for the experimental conditions employed, the degree of electrochemical reversibility varied in the pH range at which the DC polarographic data were collected. Thus, the Cd(II)–Sarcosine–OH system turned out to be a good case study to investigate applicability of the nonlinear curve–fitting models (summarized in Table 5.1 and derived from literature as described in Chapter 3 section 3.5.3) in determination of reversible half–wave potentials, $E^{r}_{1/2}$ from DC polarograms that exhibit non–reversible behaviour.

Logarithmic analyses (as described in Chapter 3, section 3.5.2.1) of selected curves at low pH (below 7.3) and high pH (above 8.5) also demonstrated that the DC curves

**Figure 5.7:** Variation in the reversibility index parameter $\delta$ 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.
below pH 7.3 could be regarded as reversible and the DC waves at higher pH values as quasi–reversible.

**Determination of** $E'_{1/2}$ **and** $I_d$

The first approach used in estimation of $E'_{1/2}$ and $I_d$ from the recorded DC polarograms was to use the Cukrowski curve–fitting method in the same fashion as it was implemented in analysis of the Cd(II)–Glycine–OH system (described in Chapter 4 section 4.4.2.1), whereby at least two curve–fitting operations were performed on each curve. The first operation generated $I_d$ values and the second one, which involved deletion of some points in the rising part of the wave and fixing of the parameter $\delta$ at a value of 1, resulted in $E'_{1/2}$ values. The second approach was to use the curve–fitting method based on Matsuda–Ayabe equation as described in Chapter 3 (section 3.5.3.2, Equation 3.44), whereby a single nonlinear curve–fitting operation was performed on a given curve to obtain directly estimates of $I_d$ and $E'_{1/2}$ values. The third and final approach was to use the Method based on Ružiće equation described in Chapter 3 section 3.5.3.3, Equation 3.49) to obtain directly $I_d$ and $E'_{1/2}$ values from nonlinear curve–fitting procedures. The set of $I_d$ and $E'_{1/2}$ values generated using these approaches were subsequently used in optimization of a metal–ligand model and determination of stability constants.

In essence, the curve–fitting methods based on the Matsuda–Ayabe and Ružiće equations, are theoretical equations with specific terms accounting for the background current, which describe the current–potential relationship in DC polarography. From a thermodynamic point of view, particularly in determination of stability constants, it is essential to know the reversible half–wave potential and limiting diffusion current. In cases where the curve–fitting models based on Matsuda–Ayabe or Ružiće equations could be successfully applied to determine $I_d$ and $E'_{1/2}$ with high accuracy, the required information to determine stability constants would be directly available.
On the other hand, from kinetics point of view, for example in kinetic studies of electrode processes, the charge transfer coefficient, $\alpha$, and the irreversible half-wave potential $E_{\text{irr}}^{1/2}$ (from the Ružić–based curve–fitting method) or $I$ (if the Matsuda–Ayabe–based curve–fitting model is used), are necessary to obtain the heterogeneous rate constants for the electrode processes under investigation.

**Figure 5.8:** Examples of analyses of DC polarograms by nonlinear curve–fitting operations to estimate $I_d$ and $E_{1/2}^r$. Circles are experimental points representing the recorded current at a particular applied potential, from a sampled DC polarographic study of Cd(II)–Sarcosine–OH system at $L_T$: $M_T = 98$, $\mu = 0.5$ M, 25 °C, initial $[M_T] = 2.035 \times 10^{-4}$ M; solid lines represent theoretically fitted curves using the curve–fitting method based on Ružić equation (Equation 3.49); dotted lines represent computed curves corresponding to fully reversible reduction processes using the $I_d$ and $E_{1/2}^r$ values obtained from the nonlinear curve–fitting operation based on Ružić equation.

Since the focus in this project was on thermodynamics rather than kinetics, applicability of the above–mentioned theoretical models in curve–fitting operations performed on DC polarograms to extract $I_d$ and $E_{1/2}^r$ values, was of foremost
importance and analysis of the kinetic parameters also obtained from the curve–fitting operations was deemed out of scope of this project.

Examples of reversible and quasi–reversible polarograms, where the reversibility index $\delta$ was 0.93 and 0.62, respectively, and the corresponding theoretical curves obtained from nonlinear curve–fitting operations utilizing the curve–fitting method based on Ružić equation, are shown in Figure 5.8.

Analysis of the $I_d$ and $E'_{1/2}$ values obtained from the three nonlinear curve–fitting approaches, the Cukrowski curve–fitting method, the method based on Matsuda–Ayabe equation and the curve–fitting method based on Ružić equation, showed that:

(a) The $I_d$ values obtained using the various curve–fitting models employed were essentially the same (negligible differences of less than 0.1 current units were observed).

(b) The $E'_{1/2}$ values obtained using the curve–fitting models based on Ružić or Matsuda–Ayabe equations, were essentially the same in the entire pH range at which the experimental DC curves were analysed. Differences of less than 0.2 mV were observed.

(c) The $E'_{1/2}$ values obtained using the curve–fitting models based on Ružić (or Matsuda–Ayabe) equations were always slightly more positive than the $E'_{1/2}$ values obtained using the Cukrowski curve–fitting method. A maximum difference of 3 mV was observed at the highest pH at which the experiment was ended, the pH corresponding to the largest decrease in electrochemical reversibility.

(d) Small differences ($< 2$ mV) between the observed half–wave potentials ($E_{1/2}$) (uncorrected for departure from electrochemical reversibility) and $E'_{1/2}$ values obtained from the various fitting procedures were observed at lower pH values ($pH < 7.5$) and the maximum difference (about 15 mV) between $E_{1/2}$ and $E'_{1/2}$ was observed at the highest pH at which the experiment was ended ($pH \approx 9.7$), the pH that corresponded to the maximum departure from electrochemical reversibility ($\delta \approx 0.6$).
A graphical comparison of the half–wave potentials obtained from the various fitting operations, together with the variation in electrochemical reversibility as a function of pH is shown in Figure 5.9.

![Graphical comparison of half-wave potentials and reversibility index](image)

**Figure 5.9:** Comparison of the observed $E_{1/2}$ values (uncorrected for departure from electrochemical reversibility) and reversible half–wave potentials ($E_{r1/2}$) obtained using different nonlinear curve–fitting models. Experimental conditions are the same as presented in Figure 5.8.

(ii) **Modelling**

Prior to any refinement operation, a reasonable metal–ligand model and suitable guesses in the stability constants for the proposed complexes must be prepared. One advantage of studying metal complexes by polarography is that graphical analysis of the variation in $I_d$ and half–wave potentials as a function of pH or free ligand concentration (Log [L]), can provide insight on the nature of complexes formed (labile or nonlabile), as well as identification of predominant metal–ligand species.
formed. General concepts in modelling of polarographic data were presented in Chapter 3 (section 3.3.2).

**Variation in limiting diffusion current with pH**

Figure 5.10 is a graph of $I_d$ as a function of pH. This graph usually provides significant information about the system studied. Basically, three relationships have been plotted in Figure 5.10. The first relationship is the observed limiting current at each $i$th pH in the presence of metal ion and ligand ($I_{(\text{comp})_{\text{pH}(i)}}$). Note that three sets of $I_d$ values, obtained from the three curve–fitting operations used in the analysis of the DC polarograms have been plotted for comparison. Indeed, negligible differences could be observed. The second relationship is the expected limiting current of the metal ion in the absence of complexes. The last relationship shown is the normalized current, i.e., the ratio $\{I_{(\text{comp})_{\text{pH}(i)}}/I_{(\text{M})_{\text{pH}(i)}}\}$. The set of $I_d$ values obtained from the Ružić–based curve–fitting method were used to generate the latter two relationships, since there was negligible differences in $I_d$ values obtained from the different fitting operations.

It is evident from Figure 5.10 that the limiting diffusion current did not vary much in the entire pH range at which experimental data were recorded (the values for normalized current varied between 1 and 0.95). This showed that the association and dissociation reactions between the metal ion, Cd(II), and the ligands (sarcosine and H$_2$O) were very fast relative to the timescale of the experimental technique employed. In other words, the Cd(II)–Sarcosine–OH system was a fully–labile metal–ligand system whereby consecutive labile complexes were formed and inert (nonlabile) species were not formed at all.
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.

Variation in half–wave potential with pH

Major metal–ligand complexes can be predicted from analysis of slopes from a plot of half–wave potentials as a function of pH. Regardless of the set of $E_{1/2}'$ used (either obtained using the Cukrowski curve–fitting method or the Ružić–based curve–fitting method); similar slopes were observed for the same range of pH for which the slopes were calculated. The set of $E_{1/2}'$ values obtained using the Ružić–based curve–fitting method were used in modelling procedures based on the analysis of slopes shown in Figure 5.11. There is no significant shift in half–wave potential up to pH of about 6.5. This might indicate the absence of cadmium complexes with sarcosine below pH 7. However, one should not exclude the possibility of the formation of M(HL) as its formation would not cause the shift in the half–wave potential.
Figure 5.11: Prediction of major metal containing species from analysis of variation in half-wave potentials as a function of pH. Experimental conditions are as indicated for Figure 5.10. The half-wave potentials used are the $E_{1/2}$ values obtained using the Ružič-based curve-fitting method.

This is because the formation of M(HL) would occur in the pH region where HL is the major form of the ligand and the reduction of M(HL) would not involve protons according to the following electrochemical process at the DME:

$$M(\text{HL}) + 2e \leftrightarrow M(\text{Hg}) + \text{HL}$$

(expected slope $\approx$ null)

Between pH 7.5 and 8.5 a slope of about 30 mV per pH unit was observed. This slope was in clear support of the formation of ML according to the following electrochemical process at the DME:

$$\text{ML} + \text{H} + 2e \leftrightarrow M(\text{Hg}) + \text{HL}$$

(expected slope of about 30 mV)

For pH above 8.5, a rather constant slope of about 55 mV per pH unit was observed. Given the fact that the predominant form of the ligand sarcosine up to pH 10 is HL (for sarcosine, the first protonation constant is 10 and the second one is 2.14), the
slope of 55 mV in the pH range above 8.5 was a strong indication of formation of ML₂. However, formation of hydroxospecies of the type ML₉(OH) could also be supported by the slope observed above pH 8.5. In the pH range between 8.5 and 10 there was already a significant fraction of the ligand in its free form L⁻ (at pH 10 there would be 50% of HL and 50% of L⁻), hence in this pH range reduction processes of the complexes may liberate the ligand in HL or L⁻ forms. Some plausible electrochemical processes at the DME would be:

\[
ML₂ + 2H + 2e \leftrightarrow M(Hg) + 2HL
\]  
(5.5) (expected slope of about 60 mV)

\[
ML(OH) + 2H + 2e \leftrightarrow M(Hg) + HL + H₂O
\]  
(5.6) (expected slope of about 60 mV)

\[
ML₂(OH) + H + 2e \leftrightarrow M(Hg) + 2L⁻ + H₂O
\]  
(5.7) (expected slope of about 30 mV)

It should be noted that the expected slope from reduction of a particular complex would be observable if that particular species existed in solution solely. Usually species form in consecutive and overlapping fashion and an observable slope would be an overall slope from all species undergoing reduction at the DME.

**Variation in half-wave potential versus free ligand concentration**

The relationship between Log [L] and half–wave potential is also very useful in identification of metal complexes of the form ML₉ by analysis of slopes as shown in Figure 5.12. A slope of about 30 mV per log unit was observed confirming unequivocally the presence of ML. Another slope of about 60 mV per log unit was observed which suggested strongly the formation of the complex ML₂ as a major species. Furthermore, a continuous increase in the slope was observed reaching a maximum value of about 80 mV per log unit. This was suggestive of the presence of
the complex ML$_3$. The expected theoretical slope for presence of ML$_3$ as predominant species is about 90 mV per log unit.

The analysis of variation on half–wave potential versus pH described above was in strong support for the formation of ML and ML$_2$. In addition, the analysis showed that the complexes M(HL) and ML$_q$(OH) (q = 1 or 2) should be tested in refinement operations. Moreover, the analysis of variation of the half–wave potential versus Log [L] strongly confirmed existence of the complexes ML and ML$_2$ and a strong suggestion for formation of ML$_3$.

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]). Experimental conditions are as indicated for Figure 5.10. The half–wave potentials used are $E'_{1/2}$ values obtained using the Ružič–based curve–fitting method.
(iii) *Optimisation of a metal–ligand model and refinement of stability constants*

The modelling procedure described above led to the following initial model: M(HL), ML, ML₂, ML₃, ML₄(OH) (q = 1 or 2), plus all known Cd(II) complexes with OH⁻. The stability constants of the Cdₓ(OH)ᵧ complexes were compiled from literature (Table 5.2A) and kept constant during refinement procedures. This initial model was then subjected to further optimisation and refinement of stability constants.

*Polarographic Complex Formation Curves*

The refinement of stability constants from the polarographic data was performed by means of the experimental and calculated complex formation curves generated using the dedicated software 3D–CFC for refinement of polarographic data (described in Chapter 3, section 3.3.1). The set of \( I_d \) and \( E_{1/2}' \) values obtained from the Ružič–based curve–fitting method were used in optimisation of a plausible metal–ligand model and refinement operations to compute stability constants. For purposes of comparing the influence of departure from electrochemical reversibility on computed stability constants, the set of \( I_d \) and observed \( E_{1/2} \) values (uncorrected for variation in electrochemical reversibility), were also used in selected refinement operations of a metal–ligand model. A summary of the outputs from the refinement procedures of the polarographic data is given in Table 5.3.

The experimental complex formation curves ECFCs, i.e. the corrected shift in half–wave potential (the right–hand side of Equation 3.10, Chapter 3) plotted versus pH are shown as points in Figure 5.13. These points constitute the experimental objective function to be reproduced by refinement operations. The calculated complex formation curve (using the \( I_d \) and \( E_{1/2}' \) values from the Ružič–based curve–fitting method) obtained for the refined stability constants for ML, ML₂, and ML₃ (Table 5.3) is shown as solid line in Figure 5.13.
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. The solid line represents the CCFC for the optimised M–L model containing ML, ML\(_2\), and ML\(_3\) with the refined stability constants given in Table 5.3.

It is reasonable to say that the experimental objective function was reproduced by the theoretical function very well. Differences between the ECFC obtained using the set of \(E_{1/2}\) values uncorrected for departure from electrochemical reversibility and the ECFC obtained from the set of reversible half–wave potentials are clearly observable in Figure 5.13. The ECFC from observed \(E_{1/2}\) could be reproduced but the computed stability constants would be higher and erroneous, particularly for the species formed at higher pH (e.g. ML\(_3\)) where the largest decrease in electrochemical reversibility was observed (see Table 5.3). This is also why the stability constants reported in the preliminary polarographic study of the Cd(II)–Sarcosine–OH system [2] were significantly larger than those values reported in this work.
A number of models could be refined by the software 3D–CFC. A systematic way of arriving to the most plausible model was to generate some species distribution diagrams for the optimised models as well as checking the models that were consistent with the analyses of slopes performed on the experimental data (Figures 5.11 and 5.12). The results confirmed some observations and conclusions made from refinement of GEP data (section 5.2.1.1). The complexes ML and ML$_2$ appeared to be the most favourite species throughout all the refinement operations; they had to be the major species in solution as predicted from analysis of slopes shown in Figures 5.11 and 5.12. Furthermore, the refined Log $\beta$ values for ML and ML$_2$ were very similar for the various models optimised.

The species M(HL) could be refined together with ML, ML$_2$, and ML$_3$, without inclusion of metal–ligand hydroxo species. However, species distribution diagram generated for the model with M(HL) showed that this species formed to a maximum fraction of 2 %. This observation led to exclusion of the complex M(HL) in further refinement operations. The possibility of existence of metal–ligand hydroxo species was also explored. The software 3D–CFC rejected the hydroxo species ML(OH) or ML$_2$(OH) when these complexes were simultaneously refined with ML, ML$_2$, and ML$_3$. The software could refine a model with ML, ML$_2$, and ML$_3$ or a model containing ML, ML$_2$, and either MLOH or ML$_2$(OH). However, the computed Log $\beta$ for MLOH (Log $\beta$ = 8.8) was rather much larger than the value expected for simple hydrolysis of ML complex. Even with the large value of log $\beta_{\text{MLOH}}$ calculated, a species distribution diagram for the model containing ML, ML$_2$ and ML(OH) showed that the species ML(OH) formed as a very minor species compared to ML$_2$. 
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. \( L_7 : M_T = 98; \) initial \([M_T] = 2.035 \times 10^{-4} \text{M}, \) at 25 °C 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. OF represents the overall fit (Equation 3.15) of complex formation curves, the computed curve in the objective experimental function

(A)

<table>
<thead>
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<th>Type of (E_{1/2}) used*</th>
<th>(\log \beta)</th>
<th>OF (± mV)</th>
<th>Remarks</th>
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<tr>
<td>(E'_{1/2})</td>
<td>M((H)L)</td>
<td>ML</td>
<td>ML(_2)</td>
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<tr>
<td>10.07 ± 0.35</td>
<td>3.804 ± 0.027</td>
<td>7.05 ± 0.03</td>
<td>8.84 ± 0.15</td>
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<tr>
<td>(E'_{1/2})</td>
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<td>6.71 ± 0.28</td>
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<tr>
<td>(E'_{1/2})</td>
<td></td>
<td>3.814 ± 0.021</td>
<td>7.04 ± 0.03</td>
</tr>
<tr>
<td>(E'_{1/2})</td>
<td>Excluded</td>
<td>3.823 ± 0.022</td>
<td>7.03 ± 0.03</td>
</tr>
<tr>
<td>Observed (E_{1/2})</td>
<td>Excluded</td>
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<td>6.94 ± 0.07</td>
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</tbody>
</table>

(B)

<table>
<thead>
<tr>
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<th>(\log \beta)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>M((H)L)</td>
<td>ML</td>
<td>ML(_2)</td>
</tr>
<tr>
<td>Results from GEP</td>
<td>Excluded</td>
<td>3.75 ± 0.01</td>
</tr>
<tr>
<td>Preliminary study</td>
<td>10.83 ± 0.05</td>
<td>4.07 ± 0.03</td>
</tr>
<tr>
<td>Literature Data</td>
<td>Not reported</td>
<td>3.88</td>
</tr>
</tbody>
</table>

*\(E_{1/2}\) obtained from Ružić–based curve–fitting method; [a] \(\mu = 0.5 \text{M}, 25 \degree \text{C}, \) Polarography; [b] Unspecified ionic strength; 25 °C, GEP
Moreover, species distribution diagrams generated using the refined stability constants for ML, ML₂, ML₃ and fixing the stability constants for ML(OH) and ML₂(OH) at the theoretical values for simple hydrolysis of ML and ML₂ complexes, respectively, showed that the species ML(OH) was a negligible species and the complex ML₂(OH) only formed appreciably at pH values above 10.5. Since the actual experimental data were collected up to pH of about 10 the inclusion of ML₂(OH) in the model was not plausible. For accurate determination of the hydroxo species more data points should have been collected beyond pH 10, but precipitation would have been the limiting factor from around pH 11.

![Species distribution as a function of pH for the Cd(II)–Sarcosine–OH system at L₇: M₇ = 98; [M₇] = 2.035 × 10⁻⁴ M. The distribution was computed using results given in Table 5.3 using the final model with ML, ML₂, and ML₃ together with all known Cdₓ(OH)ᵧ species.](image)

**Figure 5.14:** Species distribution as a function of pH for the Cd(II)–Sarcosine–OH system at L₇: M₇ = 98; [M₇] = 2.035 × 10⁻⁴ M. The distribution was computed using results given in Table 5.3 using the final model with ML, ML₂, and ML₃ together with all known Cdₓ(OH)ᵧ species.

The most plausible model, simple, with good statistical fit of the CCFC to reproduce the ECFC, and one that was consistent with the graphical analysis of slopes described earlier, was that containing ML, ML₂, and ML₃. This was taken as the final model. It
was pleasing to note that the GEP data for ML and ML\(_2\) were very much comparable to the values obtained polarographically. These results showed that the correction performed to account for departure from electrochemical reversibility by nonlinear curve-fitting of the DC polarograms, was efficient in this case.

**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). The distribution was computed using results given in Table 5.3 using the final model with ML, ML\(_2\), and ML\(_3\) together with all known Cd\(_x\)(OH)\(_y\) species.

A species distribution diagram generated for \(L_T : M_T\) ratio 98 (experimental conditions employed for the DC polarographic study of Cd(II)–Sarcosine–OH system) is shown in Figure 5.14. Clearly, the distribution shows that ML and ML\(_2\) as major species as predicted from analysis of the slopes in Figures 5.11 and 5.12. The complex ML\(_3\) formed to an appreciable amount with maximum of about 30% at pH about 9.8 where the experiment ended. However, ML\(_2\) was still the predominant species at that pH. This is consistent with the observed slope in Figure 5.12 which indicated existence of ML\(_3\) but not as the predominant species. When a species
distribution diagram was calculated for GEP conditions using the plausible model with ML, ML₂, and ML₃ from polarography, one could see that it was impossible to refine the stability constant for ML₃ from the GEP data because of precipitation that occurred when ML₃ just started to be present in the solution (Figure 5.15). Polarography helped to get the more accurate stability constant for the complex ML₃.

**Virtual Potentiometry**

Another approach used in the refinement of the polarographic data for the Cd(II)–Sarcosine–OH system was to employ the methodology of virtual potentiometry (VP) (described in Chapter 3 section 3.4). The reversible half-wave potentials obtained for each recorded polarogram at ith pH, together with the corresponding limiting diffusion currents, were converted to virtual potentials $E_{1/2}^{\text{virt}}$ using Equation 3.25 (see Chapter 3, section 3.4).

The plot of $E_{1/2}^{\text{virt}}$ versus the free metal ion concentration (obtained from refined stability constants for the optimised model containing ML, ML₂, and ML₃ – final model in Table 5.3A) generated a straight line (Figure 5.16) as expected from a real potentiometric free metal ion sensor. The $E^\circ$ and the response slope of the virtual potentiometric sensor generated from the DC polarographic data were obtained by linear fitting of the points seen in Figure 5.16, these parameters are necessary if the use of potentiometric software, such as ESTA, is of interest. The response slope obtained was close to the theoretically predicted from Nernst equation. This was in strong support of the proposed model and refined stability constants from polarography.
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, ML₂, ML₃ 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 × 10⁻⁴ M.

The program ESTA can refine data coming either from measurements of the free proton concentration (glass electrode is then used) or free metal ion concentration (either ion–selective electrode or metallic electrode might be considered). The virtual potentials generated as described above, together with the appropriate experimental conditions, were entered into the ESTA program and the stability constants for the proposed model were refined. The response slope was assumed to be according to the Nernst equation and the \( E^\circ \) was simultaneously refined with the stability constants.
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). The initial $E^{\circ}_{1/2}$(virt) set to –463.37 mV from linear fit of the $E^{\circ}_{1/2}$(virt) versus Log [M] seen in Figure 5.14.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Log $\beta$</th>
<th>$-E^{\circ}(virt)$</th>
<th>Hamilton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ML</td>
<td>ML$_2$</td>
<td>ML$_3$</td>
</tr>
<tr>
<td>VP</td>
<td>3.853 ± 0.008</td>
<td>7.03 ± 0.05</td>
<td>8.95 ± 0.05</td>
</tr>
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<td>VP &amp; GEP</td>
<td>3.78 ± 0.01</td>
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<td>9.44 ± 0.07</td>
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<tr>
<td>VP &amp; GEP</td>
<td>3.751 ± 0.009</td>
<td>6.90 ± 0.05</td>
<td>8.89$^*$</td>
</tr>
</tbody>
</table>

$^*$Fixed from DCP

One of the important capabilities of ESTA is that it allows simultaneous refinement of several titration data. Just as two or more titrations from GEP can be combined and refined simultaneously; it has been demonstrated by Cukrowski [9] that VP and GEP data can be combined and refined together. The titration data from GEP for the Cd(II)–Sarcosine–OH system were combined with the VP data generated from the DC polarographic study of the Cd(II)–Sarcosine–OH system. The VP and GEP data were refined simultaneously by ESTA. Table 5.4 provides a summary of the results obtained. It was gratifying to observe that the computed stability constants from refinement of the DC polarographic data, the refinement of GEP data and refinement of VP data were in good agreement, particularly for the complexes ML and ML$_2$. The computed Log $\beta$ value for ML$_3$ was rather large when the VP and GEP data were combined and refined together. The possible reason for the discrepancy is the fact not enough data points were available in the GEP titrations to accurately estimate the Log $\beta$ for ML$_3$ complex. Fixing the Log $\beta$ for ML$_3$ complex at 8.89 (the value computed from refinement of the DC polarographic data by the software 3D–CFC), led to reasonable stability constants for ML and ML$_2$. 

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5.2.2 Case study 2: A Lead(II)–Glycine–OH system

Several workers in the field of equilibria studies have investigated the lead–glycine system [3–4]. Main techniques used to study this system have been potentiometry (GEP and combined potentiometry using a glass electrode and a lead amalgam electrode), electrophoresis, and NMR. However, it has been noted [4] that the reported data had discrepancies and were regarded as doubtful particularly from the studies based on GEP. The main reason given was the fact that Pb(II) is hydrolysis-prone metal ion which makes it difficult to study the Pb(II)–Glycine–OH system by GEP (with GEP conditions of low $L_T:M_T$ ratios and large $M_T$ leading to a narrow pH window for collection of experimental data before precipitation takes place). Potentiometry with the use of a lead amalgam electrode (for measurements of the free Pb$^{2+}$ concentration) made it possible to lower the $[M_T]$ and collection of data up to pH of about 8 [11–12].

Even though glycine is a simple and small ligand, the speciation of this ligand with metal ions such as Pb(II), which are prone to hydrolysis, makes it rather difficult to study. The Pb(II)–Glycine–OH system was studied in this project by sampled DC polarography at several fixed $L_T:M_T$ ratios and variable pH at 25 °C and ionic strength of 0.5 M in NaNO$_3$. The Pb(II)–Glycine–OH system was re–investigated as a case study for the following main reasons: (i) to take advantage of capability of polarography as a useful and alternative technique to study metal–ligand systems at low $[M_T]$ and high $L_T:M_T$ ratios (a feature that allows to investigate such a hydrolysis–prone metal–ligand system in a wide pH range before precipitation becomes the limiting factor for collection of experimental data); (ii) to take advantage of recent methodologies for treatment of polarographic data; (iii) to take advantage of the automated instrumentation for polarographic studies of metal–ligand systems developed in this project; and (iv) as an additional case study to check applicability of the proposed curve–fitting methods for analysis of DC polarograms.
(i) **Analysis of DC polarograms and Electrochemical Reversibility**

The first step was to check for any variation in electrochemical reversibility of the sampled DC polarograms recorded. The Cukrowski curve–fitting method (described in Chapter 3, section 3.5.2.2) was implemented for nonlinear curve–fitting of the DC polarograms with linear background current with all regression parameters varied. It was found that the reversibility index parameter $\delta$ varied between 1 and 0.92 in the entire pH ranges at which data were recorded. One could regard the recorded polarograms as reversible in the entire pH range at which the experiments were done.

To check the applicability of the other nonlinear curve–fitting methods investigated in this project for extraction of $I_d$ and $E_{1/2}^r$, the method based on the Ružiĉ equation was also adopted here. The set of $I_d$ and $E_{1/2}^r$ values obtained with the Ružiĉ–based method were essentially identical to the set of $I_d$ and observed $E_{1/2}$ values obtained with the Cukrowski curve–fitting method. This observation pointed to the fact that for such reversible systems, there is no need to use other methods after the initial implementation of the Cukrowski curve–fitting method. The Cukrowski curve–fitting method provided information on electrochemical reversibility as well as the $E_{1/2}$ values (which were essentially the same as $E_{1/2}^r$) and $I_d$ values required for refinement of stability constants and optimisation of a metal–ligand model; all that information was obtained in a single nonlinear curve–fitting operation. Figure 5.17 is a graphical comparison of the $E_{1/2}^r$ obtained with the Ružiĉ–based method and the $E_{1/2}$ obtained with the Cukrowski curve–fitting method. The variation in the parameter $\delta$ obtained from the Cukrowski curve–fitting method as a function of pH is also shown on the same plot.
Figure 5.17: Comparison of the observed $E_{1/2}$ obtained using the Cukrowski curve–fitting method and $E'_{1/2}$ obtained using the Ružič-based curve-fitting. The variation in the reversibility index parameter $\delta$ 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.

(ii) **Modelling**

Modelling of the polarographic data was carried out as described in Chapter 3 section 3.3.2. The graphical analyses of the plots of limiting diffusion current $I_d$ and half-wave potentials $E_{1/2}$ as a function of pH, as well as $E_{1/2}$ as a function of free ligand concentration, were performed to allow identification of major metal–ligand complexes prior to refinement of stability constants and optimisation procedures for identification a plausible metal–ligand model. Without loss of generality, the set of $I_d$ and $E_{1/2}$ values (strictly speaking $E'_{1/2}$ values) obtained from the Cukrowski curve–fitting method was used in modelling and subsequent refinement operations.
Variation in limiting diffusion current as a function of pH

A plot of variation in $I_d$ versus pH is shown in Figure 5.18. It is clearly seen that the limiting current has decreased immediately after addition of the ligand to the solution sample containing metal ion. In the pH range between 5.2 and 6 (region I in Figure 5.18), the observed $I_d(x)$ is below the expected $I_d(o)$ for which no metal complexes are formed, and the normalised current has the constant value of about 0.95. The decrease in the limiting current after addition of the ligand and constancy in normalised current in the pH range 5 to 6 is in strong support of the formation of the complex M(HL).

This observation has been noted in a polarographic study with Cd(II)–Glycine–OH...
where formation of the species $M(HL)$ was found to correlate with the decrease in current [14].

Between pH 6 and 7.2 (region II in Figure 5.18) there is a small decrease in the normalised limiting current which reaches a constant value of about 0.85 between pH 6.5 and 7.2. This suggests formation of a labile complex. Above pH 7.2 (region III in Figure 5.18) there is a continuous decrease in the limiting diffusion current (the normalised limiting current varies from 0.8 to about 0.3). This indicates (i) formation of consecutive complexes, and (ii) the significant decrease in current indicates existence of non-labile (inert) complexes. The Pb(II)–Glycine–OH system in this case would be regarded as electrochemically reversible (fast heterogeneous kinetics, i.e., fast electron transfer) and mixed metal–ligand system with both labile and non-labile species being formed. (mixed, i.e., fast and slow homogeneous kinetics).

The significant decrease in current due to complexation necessitated the use of virtual potentials in further modelling by analysis of slopes. The use of reversible half-wave potentials, as observed directly from an experiment, in analysis of slopes is only applicable when no significant decrease in limiting current due to complexation takes place, i.e., for fully-labile metal–ligand systems [9–11].

**Variation in virtual potential as a function of pH**

Using Equation 3.25 (as described in Chapter 3, section 3.4), a set of virtual potentials $E_{1/2}^{virt}$ was generated from the sampled DCP data. Figure 5.19 shows a plot of $E_{1/2}^{virt}$ versus pH. Analysis of slopes was performed as described for the metal–ligand systems discussed in previous sections (4.4.2.1 and 5.2.1.2). The observed slopes unequivocally supported formation of the complexes $ML$ and $ML_2$. Furthermore, formation of $M(HL)$ is also supported (in the pH range 5–5.5 there is minimal shift in the potentials). Also, formation of hydroxo species of the form $ML_q(OH)_y$ should be considered. Above pH 9 the free ligand $L$ is a major form of the
ligand in solution and there is a decrease in the observed slope toward much smaller values. The complex $ML_3$ should also be considered since its formation in this pH range where the free ligand is predominant would not involve protons and no shift in potential is expected.

![Graph showing the relationship between pH and virtual half-wave potentials.](image)

**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 $LT$: $MT$ ratio 800, initial $[MT] = 8 \times 10^{-5}$ M, 25 °C and ionic strength = 0.5 M. The vertical arrow indicates the protonation constant in the pH range considered.

**Variation in virtual potential versus free ligand concentration**

In Figure 5.20 graphs of variation in the observed $E'_{1/2}$ and $E'_{1/2}(virt)$ as a function of free ligand concentration expressed as Log [L] are shown. Clearly defined slopes corresponding to formation of ML, ML$_2$, and ML$_3$ were obtained with the use of the virtual potentials $E'_{1/2}(virt)$ rather than the use of observed $E'_{1/2}$ value, the latter potentials do support formation of only ML and ML$_2$. 

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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.

(iii) Optimisation of a metal–ligand model and refinement of stability constants

The modelling procedure performed on the polarographic experimental data described above provided the following initial model: \(M(HL), ML, ML_2, ML_3, ML(OH), ML(OH)_2, ML_2(OH)\), plus all known Pb(II) complexes with OH⁻. The known stability constants for Pb(II) complexes with OH⁻ were compiled from literature [3] and kept fixed during refinement procedures. This initial model was subjected to further optimisation to arrive to the most plausible model using the software 3D–CFC as described in Chapter 3 (section 3.3.1). Polarographic complex formation curves corresponding to the refined stability constants for the most plausible model identified are shown in Figure 5.21.
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. Circles represent ECFC and the solid lines represent the CCFCs calculated using refined stability constants from the models containing $M(\text{HL})$, $ML$, $ML_2$, and $ML_3$ plus all known $\text{Pb}_x(\text{OH})_y$ species given in Table 5.5.

Table 5.5 summarises the results from the optimisation and refinement of stability constants performed on two sets of titration data from polarographic study of Pb(II)–Glycine–OH system at $L_T : M_T$ ratios 600 and 800. The high $L_T : M_T$ ratios (and low $[M_T]$) were employed to avoid early hydrolysis and precipitation so as to obtain a wide pH range for collection of experimental data. In a similar fashion as that employed in the studies of Cd(II)–Glycine–OH and Cd(II)–Sarcosine–OH discussed previously, a number of models could be refined by the software 3D–CFC and a systematic way to arrive to the most plausible model was to generate species distribution diagrams for the optimised models as well as checking for the models that were consistent with the graphical modelling of the experimental data (Figures 5.19 and 5.20).
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 °C and ionic strength, μ = 0.5 M in NaNO₃) and those reported elsewhere.

(A)

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Log β</th>
<th>Equilibrium</th>
<th>Log β</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺ + OH⁻ ↔ H₂O</td>
<td>13.74</td>
<td>Pb⁺⁺ + OH⁻ ↔ Pb(OH)⁺</td>
<td>6.00</td>
</tr>
<tr>
<td>H⁺ + L⁻ ↔ HL</td>
<td>9.54</td>
<td>Pb⁺⁺ + 2OH⁻ ↔ Pb(OH)₂</td>
<td>10.3</td>
</tr>
<tr>
<td>HL + H⁺ ↔ H₂L⁺</td>
<td>2.39</td>
<td>Pb⁺⁺ + 3OH⁻ ↔ Pb(OH)₃⁻</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2Pb⁺⁺ + OH⁻ ↔ Pb₂(OH)₃⁺⁻</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3Pb⁺⁺ + 4OH⁻ ↔ Pb₃(OH)₄⁺⁻</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4Pb⁺⁺ + 4OH⁻ ↔ Pb₄(OH)₄⁺⁻</td>
<td>35.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6Pb⁺⁺ + 8OH⁻ ↔ Pb₆(OH)₈⁺⁻</td>
<td>67.4</td>
</tr>
</tbody>
</table>

(B)

<table>
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<tr>
<th>Lᵣ : Mᵣ ratio</th>
<th>[Mᵣ] (M)</th>
<th>Log β</th>
<th>OF (± mV)</th>
<th>Refs.</th>
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<tr>
<td></td>
<td></td>
<td>M(HL)</td>
<td>ML</td>
<td>ML₂</td>
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<tr>
<td>600</td>
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<td>10.56 ± 0.04</td>
<td>4.56 ± 0.01</td>
<td>7.09 ± 0.02</td>
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<td>10.56 ± 0.04</td>
<td>4.56 ± 0.01</td>
<td>6.97 ± 0.05</td>
<td>9.0 ± 0.1</td>
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<td>10.56 ± 0.04</td>
<td>4.56 ± 0.01</td>
<td>6.99 ± 0.05</td>
<td>9.10 ± 0.06</td>
</tr>
<tr>
<td>800</td>
<td>8.053 × 10⁻⁵</td>
<td>10.45 ± 0.04</td>
<td>4.59 ± 0.01</td>
<td>7.28 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>10.46 ± 0.04</td>
<td>4.58 ± 0.01</td>
<td>7.29 ± 0.04</td>
<td>9.24 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>10.49 ± 0.03</td>
<td>4.58 ± 0.01</td>
<td>7.29 ± 0.02</td>
<td>9.25 ± 0.06</td>
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<td>Final Model*</td>
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<tr>
<td>Literature Data</td>
<td>10.50 ± 0.05</td>
<td>4.58 ± 0.01</td>
<td>7.19 ± 0.04</td>
<td>9.27 ± 0.04</td>
</tr>
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<tr>
<td>10.56[a]</td>
<td>4.6 ± 0.2[b]</td>
<td>7.5 ± 0.1[b]</td>
<td>Not reported</td>
<td>10.7[c]</td>
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<td>11.1 ± 0.1[b]</td>
<td>4.76 ± 0.07[b]</td>
<td>7.4 ± 0.1[b]</td>
<td>Not reported</td>
<td>Not reported</td>
</tr>
</tbody>
</table>

[a] μ = 1.0 M, 25 °C, Pb(Hg) ISE, Potentiometry; [b] μ = 0.5 M, 25 °C; [c] μ = 3.0 M, 25 °C, high uncertainty;
* Final Model in this work (averaged values from data for ratios 600 and 800 for the models containing M(HL), ML, ML₂, and ML₃).
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. The distribution was computed using results given in Table 5.5 with the model containing $M(HL)$, $ML$, $ML_2$, $ML_3$, and $ML_2(OH)$ together with all known $Pb_x(OH)_y$ species.

Species distribution diagrams generated for the experimental conditions employed in this work and using the refined stability constants for the models that included hydroxo species $ML(OH)$, $ML(OH)_2$ or $ML_2(OH)$ showed that the formations of the hydroxo species were negligible in the pH range at which the actual polarographic experiments were performed in this work (e.g. Figure 5.22). The computed stability constants for the hydroxo species were refined with high uncertainty (large standard deviations). It should be noted that the species $ML_3$ has not been reported in literature. Exclusion of $ML_3$ and inclusion of one of the hydroxo species in the model led to higher values of the overall fit of the ECFC onto CCFC than with the models that included $ML_3$. Since graphical modelling for the variation in half-wave potential versus Log $[L]$ (Figure 5.20) strongly showed existence of the species $ML_3$, it was plausible to include this species in optimisation procedures. It was gratifying to
observe that there was no significant effect on the computed stability constants for the complexes M(HL), ML, and ML₂ regardless of the inclusion or exclusion of the hydroxo species. From these considerations, the most plausible optimised model was found to be the one without any metal–ligand hydroxo species, i.e., the model with M(HL), ML, ML₂, and ML₃. A species distribution diagram for the plausible model is given in Figure 5.23.

The computed stability constants found for the complexes M(HL), ML, and ML₂ (complexes that have been reported previously) were in good agreement with those reported in literature [3,13]. In addition, the complex ML₃ (which has not been reported before when other experimental techniques were used) is proposed in this work where polarography was employed.

**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. The distribution was computed using results given in Table 5.5 with the model containing M(HL), ML, ML₂, and ML₃, together with all known Pbₓ(OH)ᵧ species.
Other species $\text{M(HL)}_2$ and $\text{M(HL)}_3$ have been proposed in literature [3, 12], but for experimental conditions employed in the polarographic study performed in this work, the formation of these species was considered implausible. Species distribution diagrams (e.g. Figure 5.24) generated for the total metal ion and total ligand concentrations used in this study, but using the stability constants from the literature model (which proposed the formation of the complexes $\text{M(HL)}_2$ and $\text{M(HL)}_3$ in addition to $\text{M(HL)}$, $\text{ML}$ and $\text{ML}_2$) showed that the species $\text{M(HL)}_2$ and $\text{M(HL)}_3$ formed at pH values lower than 5 and their formation would not be detectable in the polarographic study carried out in this work. The species $\text{M(HL)}_2$ and $\text{M(HL)}_3$ formed under $\text{M(HL)}$ and existed in solution to a maximum fraction of 3% at pH of about 4.5.

**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 $\text{M(HL)}$, $\text{M(HL)}_2$, $\text{M(HL)}_3$, $\text{ML}$, and $\text{ML}_2$ together with all known stability constants for Pb$_x$(OH)$_y$ complexes.
Applicability of the methodology and concept of virtual potentiometry (described in Chapter 3, section 3.4) for refinement of polarographic data (converted into virtual potentiometric data) using the dedicated potentiometric software ESTA, was also tested for the Pb(II)–Glycine–OH system. The plot of virtual potentials versus the free metal ion concentration (obtained from refined stability constants for the optimised model containing M(HL), ML, ML₂, and ML₃ in Table 5.5) generated a straight line (Figure 5.25). The response slope obtained was close to that predicted from Nernst equation. This was in strong support of the proposed model and refined stability constants from polarography.

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, ML₂, ML₃ for the Pb(II)–Glycine–OH studied by sampled DC polarography at Lₜ : Mₜ = 600, ionic strength = 0.5 M, 25 °C, initial [Mₜ] = 8.062 × 10⁻⁵ M.

\[ y = 28.479x - 257.95 \]
\[ R^2 = 0.9995 \]
The virtual potentials generated from the polarographic data, together with the appropriate experimental conditions were entered into the program ESTA and the stability constants for the proposed model were refined. Difficulties in refinement were encountered by the program ESTA if all the stability constants for the proposed model were allowed to be refined. It should be realized, however, that the experimental conditions employed (high \( L_T : M_T \) ratio) were not typical for potentiometry. The high \( L_T : M_T \) ratios employed was likely to be the cause of the difficulties experienced in refinement operations performed using the potentiometric software ESTA. However, fixing the stability constants for M(HL) and/or ML obtained from the refinement of the polarographic data (Table 5.5), and simultaneously refining the initial \([H^+]\) and the \( E^\circ \), led to reasonable refinement of the stability constants for the complexes ML\(_2\) and ML\(_3\). Some results from the refinement operations using virtual potentiometric data for the Pb(II)–Glycine–OH system are shown in Table 5.6.

**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). The initial \( E^\circ(virt) \) set to –257.95 mV from linear fit of the virtual potentials versus Log [M] seen in Figure 5.25. Initial \([H^+]\) was 0.0000001 M.

<table>
<thead>
<tr>
<th>Log ( \beta )</th>
<th>M(HL)</th>
<th>ML</th>
<th>ML(_2)</th>
<th>ML(_3)</th>
<th>( -E^\circ(virt) )</th>
<th>Refined [H(^+)] (M)</th>
<th>Hamilton R–Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10.5^* )</td>
<td>4.36 ± 0.02</td>
<td>7.58 ± 0.01</td>
<td>8.6 ± 0.1</td>
<td>252.67</td>
<td>0.000149</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>( 10.5^* )</td>
<td>4.56</td>
<td>7.54 ± 0.03</td>
<td>9.0 ± 0.1</td>
<td>251.48</td>
<td>0.000170</td>
<td>0.003</td>
<td></td>
</tr>
</tbody>
</table>

*Stability constants obtained from DCP experiments and fixed here during the refinement operations.*
Case study 3: A Lead(II)–Sarcosine–OH system

It was noted in the introductory part of this chapter that no literature data were found for the solution chemistry of the Pb(II)–Sarcosine–OH system, with hydrolysis being the primary limitation, for instance, to employ the most widely used potentiometric techniques to study the Pb(II) metal–ligand system. However, polarography was found to be a useful alternative experimental technique for the solution chemistry study of the Pb(II)–Sarcosine–OH system and a preliminary study [2] indicated that polarography could be useful in avoiding hydrolysis at high pH, with a clear possibility to widen the pH window for collection of experimental data.

Armed with a unique automated instrumental set–up for sampled DC polarography developed in this project (described in Chapter 4), modern methodologies for treatment of polarographic data for optimisation of a metal–ligand model and refinement of stability constants (described in Chapter 3), as well as, the curve–fitting models for rigorous analysis of DC polarograms (summarised in Table 5.1 section 5.1), the solution chemistry of Pb(II)–Sarcosine–OH system was investigated by sampled DC polarography at fixed $L_T:M_T$ ratio of 400 (in the pH range 5 to 10, at fixed ionic strength of 0.5 M, at 25 °C and in NaNO$_3$ aqueous medium).

(i) Analysis of DC Polarograms and Electrochemical Reversibility

The DC polarograms collected were firstly analysed using the Cukrowski curve–fitting method (Chapter 3, section 3.5.2.2) to elucidate the degree of electrochemical reversibility for the Pb(II)–Sarcosine–OH system. Unlike in the case of the previous metal–ligand systems investigated in this work, whereby a linear function of the form $I_b = a + bE_{appl}$ was used successfully to account for the background current in the recorded polarograms, the background current for the curves in the pH range 5 to 8 in the case of Pb(II)–Sarcosine–OH system was found not to vary in a perfectly linear manner. Thus, a polynomial function of the form $I_b = a + bE_{appl} + cE_{appl}^2$, was found
to be a better function to account for the background current in nonlinear curve–fitting operations performed on the curves recorded in the pH range 5 to 8. For the rest of the polarograms, the usual linear function was found to be sufficient.

In the pH range 5 to 10 (the full experimental for the DC polarographic data), the reversibility index parameter $\delta$ (obtained from each recorded polarogram using the Cukrowski curve–fitting method) varied from 1 to 0.65. Thus, in the case of Pb(II)–Sarcosine–OH system, for the experimental conditions employed, the degree of electrochemical reversibility varied from reversible to quasi–reversible in the pH range at which the DC polarographic data were recorded. Consequently, the nonlinear curve–fitting methods based on Matsuda–Ayabe and Ružić equations (described in Chapter 3, section 3.5.3.2 and summarised in Table 5.1 section 5.1) were employed to determine the $I_d$ and $E_{1/2}$ in a similar fashion as described for the Cd(II)–Sarcosine–OH system.

For the curves in the pH range 5 to 8, as noted above the use of a linear function to account for the background current was not plausible. It was observed that the nonlinear curve–fitting models based on Matsuda–Ayabe and Ružić equations were very sensitive to the nature of the background current as the use of inappropriate function that did no produce a good fit on the background current led to erroneous $E_{1/2}'$ values and difficulties in convergence. The use of the polynomial function of the form $I_b = a + bE_{appl} + cE_{appl}^2$, to account for background current resulted in successful convergence, better fits, and reliable $E_{1/2}'$ (a smooth function of $E_{1/2}'$ versus pH was observed). The usual linear background current function was found to be applicable and sufficient in the fitting of the curves above pH 8.

As it was observed in the case of Cd(II)–Sarcosine–OH system (section 5.2.1.2), in the case of Pb(II)–Sarcosine–OH system the use of Ružić–based curve–fitting model and the model based on Matsuda–Ayabe equation led to essentially the same values of $I_d$ and $E_{1/2}'$ values. Examples of reversible and quasi–reversible DC polarograms
analysed using the Ružić–based curve–fitting method are shown in Figure 5.26. For all the curves analysed, the $E'_{1/2}$ values were computed with high certainty (standard deviations of less than ± 0.5 mV were typically obtained from the nonlinear curve–fitting operations).

![Graph showing examples of analyses of DC polarograms from a sampled DC polarographic study of Pb(II)–Sarcosine–OH system at $L_T : M_T = 400$, $\mu = 0.5$ M, 25 °C, $[M_T] = 7.990 \times 10^{-5}$ M. Circles are experimental points representing the recorded current at a particular applied potential; solid lines represent theoretically fitted curves using the curve–fitting method based on the Ružić equation (Equation 3.49); dotted lines represent computed curves corresponding to fully reversible reduction processes using the $I_d$ and $E'_{1/2}$ values obtained from the nonlinear curve–fitting operation based on Ružić equation.]

**Figure 5.26:** Examples of analyses of DC polarograms from a sampled DC polarographic study of Pb(II)–Sarcosine–OH system at $L_T : M_T = 400$, $\mu = 0.5$ M, 25 °C, $[M_T] = 7.990 \times 10^{-5}$ M. Circles are experimental points representing the recorded current at a particular applied potential; solid lines represent theoretically fitted curves using the curve–fitting method based on the Ružić equation (Equation 3.49); dotted lines represent computed curves corresponding to fully reversible reduction processes using the $I_d$ and $E'_{1/2}$ values obtained from the nonlinear curve–fitting operation based on Ružić equation.

Figure 5.27 is a graphical comparison of the reversible half–wave potentials $E'_{1/2}$ (obtained using the Ružić–based curve–fitting method) and the observed half–wave potential $E_{1/2}$ (obtained using the Cukrowski curve–fitting method without correction
for departure from electrochemical reversibility). The variation in electrochemical reversibility (as indicated by the reversibility index parameter $\delta$) is also plotted in Figure 5.27. The differences between the observed $E_{1/2}$ and $E'_{1/2}$ were negligible below pH 6 (where essentially reversible electrochemical processes took place) and became significant (differences of up to 10 mV) at pH above 6 where quasi-reversible electrochemical processes were observed. Without loss of generality the $I_d$ and $E'_{1/2}$ obtained with the Ružić-based curve-fitting method were subsequently used in modelling and refinement operations to determine a plausible metal–ligand model and the corresponding stability constants.

**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. The corresponding variation in electrochemical reversibility (a plot of $\delta$ as a function of pH) is also shown.
Modelling of the experimental data was carried out in the same fashion as described for the other metal–ligand systems discussed in previous sections in this work (sections 5.2.1.2 and 5.2.3) whereby graphical analyses of the plots of limiting diffusion current \( I_d \) and reversible half–wave potential versus pH or Log[L] were performed (Figures 5.28, 5.29, and 5.30).

The variation in the \( I_d \) as a function of pH (Figure 5.28) clearly indicated formation of lead complexes with both labile and non–labile species being present (the normalised limiting current varied from 1 to about 0.6). The decrease in the \( I_d \) upon addition of the ligand suggested presence of the complex M(HL) (This feature was also observed in the case of the Pb(II)–Glycine–OH system discussed in section 5.2.3).

![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 \( L_T : M_T = 400, [M_T] = 7.990 \times 10^{-3} \text{ M, } 25 \, ^\circ\text{C, } \mu = 0.5 \text{ M. (} \square \text{) represent the expected limiting diffusion current (a decrease is caused by dilution); (x) represent the observed limiting diffusion current (a decrease is caused by formation of lead complexes); (o) represent the normalised limiting current (the ratio of observed } I_d \text{ and expected } I_d \).}](image-url)
The decrease in the limiting current also necessitated the use of virtual potentials $E'_{1/2(\text{virt})}$ (computed as described in Chapter 3 section 3.4) in analysis of shifts in $E'_{1/2}$ versus pH and Log [L] (Figures 5.29 and 5.30). Analyses of the slopes in Figures 5.29 and 5.30 clearly supported formation of the complexes ML and ML$_2$ and indicated formation of the complex ML$_3$ (slopes of more than 70 mV per log unit or pH unit were observed). Moreover, formation of M(HL) should be considered (no shift of $E'_{1/2(\text{virt})}$ in the pH range 5 to 6.5 was observed and formation of M(HL) would not involve protons in this pH range where the ligand sarcosine existed 100% in the HL form). An increase in slope from 55 to 85 mV per pH unit was observed in the pH range above 8.5 (Figure 5.29). This increase in slope at higher pH prompts one to consider formation of hydroxo species of the type ML$_x$(OH)$_y$ (with x,y = 1 or 2) in addition to an indication of formation of the complex ML$_3$.

**Figure 5.29:** Variation in virtual half–wave potential as a function of pH for the Pb(II)–Sarcosine–OH system. Experimental conditions as in Figure 5.28.
From graphical modelling of the experimental data, the initial model considered for further optimisation consisted of M(HL), ML, ML₂, ML₃ and the hydroxo species ML(OH), ML(OH)₂, ML₂(OH), and ML₂(OH)₂ were also considered. All known Pb(II) complexes with OH⁻ were included in all refinement operations and their stability constants (compiled from literature [3]) were kept fixed during the refinement procedures. The software 3D–CFC (described in section 3.3.1 of Chapter 3) was employed for further optimisation of the initial model and refinement of stability constants with the final aim of arriving to a plausible metal–ligand model. A summary of the results of the refinement procedures is shown in Table 5.7. Refinement of the model containing M(HL), ML, ML₂, and ML₃, with exclusion of hydroxo species of the form MLₓ(OH)ᵧ (x, y = 1 or 2), led to a rather poor fit of the calculated complex formation curve (CCFC) onto the experimental complex formation curve (ECFC). This showed that the hydroxo species should be considered.
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 LT : MT = 400; initial [M] = 7.990 × 10–5 M, at 25 °C and μ = 0.5 M in NaNO3.

(A)

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(B)

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<tr>
<td></td>
<td>10.98 ± 0.03</td>
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</table>

[a] μ = 0.5 M, 25 °C, Polarography.
Exclusion of the species M(HL) also led to poor fit of the CCFC onto ECFC. The software 3D–CFC could not successfully refine any model containing M(HL), ML, ML₂, ML₃, together with any of the hydroxo species ML(OH), ML(OH)₂, or ML₂(OH). The only plausible model containing M(HL), ML, ML₂, ML₃, and a hydroxo species that was successfully refined with a good fit of the CCFC onto the ECFC was the one that included the species ML₂(OH)₂. Species distribution diagram computed for this model (Figure 5.31) was consistent with the graphical modelling performed in prediction of major metal–ligand species (Figures 5.29 and 5.30).

![Figure 5.31: Species distribution as a function of pH for the Pb(II)–Sarcosine–OH system generated for L₇ : M₇ = 400 and [M₇] = 8 × 10⁻³ M (conditions employed in this work) using the stability constants for the model containing M(HL), ML, ML₂, ML₃, and ML₂(OH)₂, together with all known stability constants for Pbₙ(OH)ₙ complexes. The stability constants used are given in Table 5.7.](image)

The species ML₃ formed as a minor species (maximum fraction of about 15% in solution when compared to the species ML, ML₂, and ML₂(OH)₂). This would explain, for instance, why the maximum observed slope in analysis of variation in
$E'_{1/2}(virt)$ versus Log [L] (Figure 5.30) was about 70 mV per Log unit. If ML$_3$ formed as a major species then a slope closer to the theoretically expected value of 90 mV per Log unit should have been observed. However, the observed slope was above 60 mV per Log unit clearly suggesting co–existence of the species ML$_2$ and ML$_3$ with ML$_2$ being predominant. The final model was taken as the one containing M(HL), ML, ML$_2$, ML$_3$ and ML$_2$(OH)$_2$ with the final computed stability constants as shown in Table 5.7.

The use of observed $E_{1/2}$ values (uncorrected for departure from electrochemical reversibility) clearly showed how erroneous the computed stability constants can become (see Table 5.7) if one does not correct for decrease in electrochemical reversibility. This could also have been the case in the preliminary study of Pb(II)–Sarcosine–OH [2]. For instance, the value for Log $\beta_{ML}$ was computed as 4.49 in the preliminary study, a value that was rather large compared to the one obtained with the use of reversible half–wave potentials in this work.

The use of virtual potentiometry in refinement of the polarographic data was not plausible with similar difficulties as were encountered in the case of Pb(II)–Glycine–OH system. Once again the high L$_T$ : M$_T$ ratio employed in the polarographic study of Pb(II)–Sarcosine–OH system in this work was the limiting factor for any successful refinement of the virtual potentiometric data by the dedicated potentiometric software ESTA. The high L$_T$ : M$_T$ ratio employed was found to be necessary in this work to avoid hydrolysis.

5.2.4 Case study 4: A Zinc(II)–Glycine–OH system

The Zn(II)–Glycine–OH system has been extensively studied, mainly with the glass electrode potentiometry (GEP), and reliable data are available in literature at various temperatures, media, and ionic strengths [3–4]. Polarographic methods have scarcely been employed to investigate the coordination equilibria of Zn(II)–Glycine–OH
system due to the difficulty presented by the accurate analysis of quasi–reversible waves. Polarographic studies reported in the literature have been confined to studies at fixed pH and variable ligand concentration and the polarographic data were analysed with the traditional graphical methods (logarithmic analyses) in determination of reversible $E_{1/2}$ and kinetic parameters of the electrode processes [15–18] as well as attempts in computation of stability constants [19–21] using the DeFord and Hume [22] or Schaap and McMasters [23] methods.

In this work the Zn(II)–Glycine–OH system was studied using GEP and sampled DC polarography at fixed $L_T : M_T$ ratio and variable pH at 25 °C and ionic strength of 0.5 M in NaNO$_3$ aqueous medium. The Zn(II)–Glycine–OH system was investigated as the last case study with regards to applications and limitations of the nonlinear curve–fitting procedures derived from literature and tested in this work for analysis of non–reversible DC polarograms collected in DC polarographic studies of metal–ligand systems. It is generally known that the reduction of Zn(II) is non–reversible (with quasi–reversible to fully irreversible DC waves being typically encountered) [15–21]. The Zn(II)–Glycine–OH system was considered a good candidate to further test the applicability and limitations of the nonlinear curve–fitting methods derived in this work to account for variation in electrochemical reversibility. The main focus in this work, of course, was analysis of polarographic data. However, it was considered reasonable to re–establish the literature data by studying the Zn(II)–Glycine–OH system by GEP with the GEP results to be used for direct comparison with the polarographic data.

### 5.2.4.1 A GEP study of a Zn(II)–Glycine–OH system

Glass electrode potentiometric experiments were performed for the Zn(II)–Glycine–OH system at $L_T : M_T$ ratio 1 : 1 (pH data acquired between pH 4.5 and 7.7 with precipitation occurring at about pH 8) and at $L_T : M_T$ ratio 6 : 1 (pH data acquired between pH 5 and 9.7, precipitation at about pH 10). The ESTA suite of programs
(described in Chapter 3, section 3.2) was used for refinement and optimisation procedures in determination of stability constants for plausible metal complexes. Experimental data and outputs of the refinement operations from ESTA programs have been documented in Appendix G. The data from the two titrations were initially refined independently and thereafter combined and optimised simultaneously to arrive to a plausible final model.

In the refinement operations performed, different models containing M(HL), ML, ML₂, ML₃, and ML(OH) were tested. A summary of the refinement results from the analysis of GEP data are shown in Table 5.8. The complex M(HL) could be refined in some instances but species distribution diagram for the model considered and generated using the computed stability constants showed that the species M(HL) was negligible for the experimental conditions employed (with maximum of 3% for the ratio 6 experimental conditions). The species M(HL) was then excluded from further optimisation procedures. The stability constants for the species ML, ML₂, ML₃, and ML(OH) were favourably refined with very good agreement with the value reported in the databases of critically evaluated stability constants [3–4]. The final model was taken from simultaneous refinement of the two titration data (Lₜ : Mₜ ratios 1 and 6 combined) and consisted of the species ML, ML₂, ML₃, and ML(OH).

Values of the complex formation function ZBAR(M) versus pL, represented in Figure 5.32, were calculated for each datum point using the ESTA program as described in section 3.2 of Chapter 3. The ZBAR(M) function clearly showed formation of complexes ML, ML₂, and ML₃. ML₂ was a major species in solution for the experimental conditions at Lₜ : Mₜ ratio 6 : 1 (ZBAR(M) value of about 2 was observed in a wide pL range). ZBAR(M) values above 2 and approaching 3 clearly showed existence of ML₃ as a significant species in solution.
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 °C and ionic strength, χ = 0.5 M in NaNO₃) and those reported elsewhere.

(A)

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<th>Equilibrium</th>
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<td>H⁺ + OH⁻ ↔ H₂O</td>
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<td>Zn⁺⁺ + OH⁻ ↔ Zn(OH)⁺</td>
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<td>H⁺ + L⁻ ↔ HL</td>
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<td>4.85 ± 0.04</td>
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* Final model from GEP in this work; [a], [b] χ = 0.5 M, 25 °C, Mean values from several potentiometric techniques; [c] χ = 0.15 M, 37 °C
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 × 10^{-3} M, 25 °C, and μ = 0.5 M. The complex formation curves were obtained using the final metal–ligand model containing ML, ML\_2, ML\_3, and ML(OH) with the optimized stability constants for these complexes shown in Table 5.8.

Species distribution diagrams (Figures 5.33 and 5.34) for the Zn(II)–Glycine–OH system were generated for the experimental conditions employed in the GEP studies. Clearly, the species distribution diagrams showed that the species ML, ML\_2, ML\_3 and ML(OH) were formed in significant amounts to provide enough experimental information for their identification and computation of the relevant stability constants as was found in this case. The species distribution diagram generated for L_T : M_T ratio 1 : 1 experimental conditions (Figure 5.33) showed that the complexes ML, ML\_2, and ML(OH) formed appreciably in the pH range at which data were collected (pH 4.5 to 7.7). The species distribution diagram generated for L_T : M_T ratio 6 : 1 (Figure 5.34) clearly showed that the species considered for the final model (ML, ML\_2, ML\_3, and ML(OH)) were formed significantly in the pH range at which data were collected (pH 5 to 9.8) and supported the fact that the final model was very plausible indeed.
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, \([M_T] = 9.838 \times 10^{-3} \text{ M} \). The distribution was computed using results given in Table 5.8 using stability constants from the final model containing ML, ML\(_2\), ML\(_3\), and ML(OH) together with all known Zn\(_x\)(OH)\(_y\) species from the combined refinement.

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, \([M_T] = 1.096 \times 10^{-3} \text{ M} \). The distribution was computed using results given in Table 5.8 using stability constants from the final model containing ML, ML\(_2\), ML\(_3\), and ML(OH) together with all known Zn\(_x\)(OH)\(_y\) species from the combined refinement.
5.2.4.2 Polarographic Investigations of a Zn(II)–Glycine–OH System

Sampled DC polarography was employed to study the Zn(II)–Glycine–OH system at fixed \( L_T : M_T \) ratio of about 200 in the pH range 5 to 11.

(i) **Analysis of DC Polarograms and Electrochemical Reversibility**

The polarography of Zn(II) in the presence of glycine was found to be different from that of Cd(II) and Pb(II) discussed in previous sections. In the cases of Cd(II) and Pb(II), a single DC wave was observed that shifted to more negative potentials with increasing pH and with decrease in the limiting diffusion current due to complexation and/or dilution. Typical polarograms recorded for the Zn(II)–Glycine–OH system are shown in Figure 5.35. With Zn(II)–Glycine–OH system, a single DC wave was observed for the Zn\(^{2+} \) in the absence of glycine (i.e. ‘free’ Zn\(^{2+} \)) at about –0.9 V and in the presence of glycine the single wave (which will hereafter be referred to as the first wave) was observed shifting to more negative potentials in the pH range 4.5 to about 6. At pH of about 6 a second wave appeared at potentials of about -1.15 and -1.2 V. With increasing pH the height of the first wave decreased and the first wave continued to shift to more negative potentials and the height of the second wave increased with increasing pH. With further increase in pH (above pH 7.6) the two waves overlapped significantly (not completely resolved) and eventually at pH above 9 the first wave disappeared completely (or fully overlapped with the second wave) and a single wave was observed again up to the last pH at which data were collected (pH of about 10.7).

A literature survey of voltammetric studies of Zn(II) in the presence of glycine revealed that the double waves observed at some pH range have indeed been encountered previously [15–21]. The appearance of two DC waves for the Zn(II)–Glycine–OH system has been attributed to either two types of complexes between which equilibrium is slowly established or to inadequate buffering by the excess glycine or to both cases. The buffering effect has been investigated by addition of an
external buffering agent at various pH and two waves could still be observed and hence, coexistence of two or more types of zinc complexes, between which equilibrium is slowly established, was the main factor attributed to the observation of two DC waves in polarographic studies of the Zn(II)–Glycine–OH system [15, 17, 19–20].

![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. Data were collected for the following experimental conditions: Initial \[M_T\] = 1 × 10^{-4} M, \[L_T : M_T = 240, \mu = 0.5 \text{ M} \] and 25 °C.](image)

In order to link the observed polarograms for the Zn(II)–Glycine–OH system in this work with the existence of two or more types complexes in slow equilibrium in solution, species distribution as a function of pH for the metal–ligand system was generated for the experimental conditions employed in this work (see Figure 5.36) using the final model and stability constants re-established in this work for the Zn(II)–Glycine–OH system by the independent analytical technique GEP (Table 5.8).
The species distribution as a function of pH showed that formation of the ML complex began at pH of about 4 and the complex ML existed as a sole metal–ligand complex in solution up to pH of about 5.8 at which point the complex ML\textsubscript{2} began to form.

**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\textsubscript{T} : M\textsubscript{T} = 240 : 1; [M\textsubscript{T}] = 1.07 \times 10^{-4} \text{ M}). The species distribution was computed using the final model obtained from the GEP study of the Zn(II)–Glycine–OH system (Table 5.8).

The complexes ML and ML\textsubscript{2} co–existed in solution up to pH of about 7.2 where ML\textsubscript{3} began to form in solution. From the species distribution, it qualitatively follows that the single DC wave observed in the pH range 5 to 6 was due to reduction of the ML complex and the second wave that started to appear at pH of about 6 was due to reduction of ML\textsubscript{2} which was in slow homogeneous equilibrium with ML in the polarographic timescale employed. Since this second wave grew in height and fully overlapped with the first wave at pH of about 9 (the pH at which species distribution showed that the ML complex was practically absent in the bulk of the solution), this
could as well mean that the second wave above pH 7 was also due to reduction of both ML$_2$ and ML$_3$, both species being in slow homogeneous equilibrium with ML. In summary, the electrode reactions of Zn(II)–Glycine–OH system can be expressed by the following illustrative scheme:

\[
\begin{align*}
\text{Zn}^{2+} & \xleftrightarrow{\text{fast}} \text{ZnL}^+ \xleftrightarrow{\text{slow}} \text{ZnL}_2 \xleftrightarrow{} \text{ZnL}_3 \\
\downarrow \text{+2e} & \quad \downarrow \text{+2e} \quad \downarrow \text{+2e} \quad \downarrow \text{+2e}
\end{align*}
\]

\[\text{Zn(Hg)}\]

Having provided the qualitative explanation for the observation of double waves in some pH range in the polarographic study of the Zn(II)–Glycine–OH system, the next step was to adopt nonlinear curve–fitting procedures, (i) to elucidate the degree of electrochemical reversibility involved on the recorded polarograms, and (ii) if possible, to extract appropriate $I_d$ and $E_{1/2}$ values for subsequent use in refinement of stability constants.

**Analysis of the single DC curves below pH 6 and above pH 9**

In order to determine the nature of electrochemical reversibility of the single DC polarogram recorded below pH of about 6, the usual Cukrowski curve–fitting method (Equations 3.32–3.33, described in section 3.5.2.2 of Chapter 3) was employed. The linear function was used to account for the background current. It was found that the reversibility index coefficient $\delta$ was 0.82 for the polarogram of Zn(II) in the absence of glycine and for the single polarograms recorded in the presence of glycine at various pH values $\delta$ varied between 0.82 and 0.75. Logarithmic analysis (as described in section 3.5.2.1 of Chapter 3) of selected curves recorded below pH 6 showed curved plots of $\text{Log}(I_{\text{red}}/I_d-I_{\text{red}})$ versus $-E_{\text{appl}}$ indicating that the polarograms below pH 6 were quasi–reversible. These observations confirmed that the reduction
processes of Zn(II) in the absence and presence of glycine for the single DC waves observed below pH 6 were quasi–reversible. For the quasi–reversible curves below pH 6, the Ružič–based and Matsuda–Ayabe based curve–fitting methods were then employed to extract \( I_d \) and \( E_{1/2}^r \). The set of \( I_d \) and \( E_{1/2}^r \) found by the two methods were essentially the same. An example of a fitted DC curve recorded below pH 6 and the constructed reversible wave are shown in Figure 5.37.

![Figure 5.37: An example of analysis of a quasi–reversible DC polarogram from a DCP study of a Zn(II)–Glycine–OH system collected below pH 6 at \( L_T : M_T = 240, 25 \, ^\circ C, \mu = 0.5 \, M \) and initial \([M_T] = 1.07 \times 10^{-4} \, M\). Circles represent experimental points of recorded currents at particular applied potentials; the solid curve represents the fitted curve using the nonlinear curve–fitting method based on the Ružič equation (Equation 3.49); the dotted line represent the computed curve corresponding to fully reversible reduction process using the \( I_d \) and \( E_{1/2}^r \) values obtained from the nonlinear curve–fitting operation based on the Ružič equation. Observed \( E_{1/2}^r \) and \( \delta \) obtained from curve–fitting performed on the same curve are from the Cukrowski method (Equation 3.33).](image)

The single DC curve obtained above pH 9 was also fitted using the Cukrowski method; due to \( H_2 \) gas evolution, the exponential function (Equation 3.35) was used.
to account for the background current. $\delta$ was obtained in the range 0.6–0.65, which indicated non–reversible nature of the waves above pH 9. The curves above pH 9 were further re–fitted using the Ružić–based and Matsuda–Ayabe based curve–fitting methods. With the curve–fitting procedure based on Matsuda–Ayabe equation, no successful convergence was found for the irreversible waves considered. With the use of Ružić–based curve–fitting procedure as seen in Figure 5.38, it was possible to theoretically reproduce the irreversible DC curves at high pH values. The irreversible nature of those curves was further confirmed by logarithmic analysis (e.g. Figure 5.39) whereby a straight line with non–Nernstian slope was observed.

![Figure 5.38](image)

**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. Observed $E_{1/2}$ and $\delta$ obtained from curve–fitting performed on the same curve shown using the Cukrowski method (Equation 3.33).
Some important observations were made on the parameters obtained from fitting the irreversible waves above pH 9 with the Cukrowski and the Ružič–based curve–fitting methods: (i) the $I_d$ values obtained were essentially the identical, (ii) the observed $E_{1/2}$ from the Cukrowski curve–fitting method was essentially identical to the $E_{1/2}^{irr}$ generated by the Ružič–based curve–fitting procedure, (iii) $\alpha$ from Cukrowski method was exactly the same as $\alpha$ obtained with the Ružič–based curve–fitting procedure (iv) the Ružič–based curve–fitting procedure generated $E_{1/2}'$ values at potentials over 100 mV more positive than the observed $E_{1/2}$, but with large statistical uncertainty (standard deviations of ± 0.1 V); the difference in potentials can be regarded as huge and the $E_{1/2}'$ generated meaningless. These observations led to the following conclusion; for irreversible waves, the parameters $I_d$, $\alpha$, and $E_{1/2}^{irr}$ are statistically and physically significant to theoretically reproduce a given DC wave by curve–fitting.
Analysis of double waves in the pH range 6–9

To resolve the closely spaced waves observed in the pH range 6–9, by nonlinear curve–fitting, the curve–fitting method requires that a constructed current–potential relationship be closely matched to the experimental polarogram which arises from the reduction of two or more complexes that have distinct half–wave potentials. The fundamental assumption underlying the resolution of overlapped waves by curve–fitting is that the two reductions do not interact in any way. The observed current–potential curve involving the sum of two independent reduction waves can be expressed as:

\[ I_{\text{obs}} = I_{\text{red,1}} + I_{\text{red,2}} + I_b \]  \hspace{1cm} (5.8)

where \( I_{\text{obs}} \) is the total current recorded at a particular applied potential, \( I_{\text{red,1}} \) and \( I_{\text{red,2}} \) are the reduction currents corresponding to the first wave and the second wave, respectively, and \( I_b \) is the background current.

In an attempt to extract \( I_d \) and \( E_{1/2} \) values from the first wave, the double waves in the pH range 6 to 9 were fitted using modified versions of the Cukrowski and the Ružić–based curve–fitting methods (Equations 5.9 and 5.10). Equations 5.9 and 5.10 were used as regression equations that accounted for two individual reduction processes.

\[
I_{\text{obs}} = \frac{I_{d_1}}{\exp \left( \frac{\delta n F}{RT} (E_{\text{appl}} - E_{1/2,1}) + 1 \right)} + \frac{I_{d_2}}{\exp \left( \frac{\delta n F}{RT} (E_{\text{appl}} - E_{1/2,2}) + 1 \right)} + I_b \quad (5.9)
\]

(The Cukrowski curve-fitting method adopted for resolving two waves)
\[
I_{\text{obs}} = \frac{I_{d,1}}{\exp \left( \frac{\alpha \cdot nF}{RT} \left( E_{\text{app},1} - E_{1/2,1}^{\text{irr}} \right) \right) + \exp \left( \frac{nF}{RT} \left( E_{\text{app},1} - E_{1/2,1}^{r} \right) \right) + 1} + \frac{I_{d,2}}{\exp \left( \frac{\alpha \cdot nF}{RT} \left( E_{\text{app},2} - E_{1/2,2}^{\text{irr}} \right) \right) + \exp \left( \frac{nF}{RT} \left( E_{\text{app},2} - E_{1/2,2}^{r} \right) \right) + 1} + I_b
\] (5.10)

(The Ružić–based curve–fitting method adopted for resolving two DC waves)

In equations 5.9 and 5.10, \( I_{d,i}, E_{1/2,i}, \alpha_i, \delta_i, E_{1/2,i}^{\text{irr}}, \) and \( E_{1/2,i}^{r} (i = 1 \text{ and } 2) \) are the regression parameters corresponding to the individual waves being resolved by nonlinear curve–fitting.

**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 \( [M_T] = 1.07 \times 10^{-3} \text{ M} \), curve recorded at pH 7.091. Circles represent experimental points of recorded currents at particular applied potentials; the solid line represent the fitted curve obtained by nonlinear curve–fitting employing Equation 5.10; dotted lines represent the individual reduction waves each computed with the Ružić equation (Equation 3.47) using parameters obtained from curve–fitting.
An example of a fitted curve using the modified Ružić–based curve–fitting method is shown in Figure 5.40. The resolution of the two waves by curve–fitting was done up to pH of about 7.5. The curves recorded in the pH range 7.5 to about 9 were significantly overlapped and any attempt to resolve them by curve–fitting was implausible.

(ii) **Refinement of stability constants**

From analysis of the DC curves by curve–fitting, the following sets of data were extracted for consideration in refinement operations: (i) $I_d$ and $E_{r1/2}$ from the quasi–reversible first wave observed below pH 6, (ii) $I_d$ and $E_{r1/2}$ from the first wave extracted by resolving the two overlapping waves in the pH range 6 to 7.5, (iii) $I_d$, $E_{r1/2}$, and $E_{irr1/2}$ extracted from the single irreversible DC wave observed above pH 9.

To gain insight on whether these sets of data were of any use in computation of stability constants, experimental complex formation curves (ECFCs) were generated from the data and the ECFCs were directly compared to the calculated complex formation curve (CCFC) generated for the full metal–ligand model determined independently by GEP (the final model in Table 5.8) but using the same experimental conditions for which the ECFCs from the DCP experiment were computed (see Figure 5.41).

It became evident from the inspection of the polarographic complex formation curves that the experimental points generated from the first wave up to pH of about 6 followed the expected complex formation curve (the CCFC generated with GEP results) reasonably well but the points increasingly departed from the CCFC in the pH range 6 to 7.5 where the second wave became more pronounced. This observation strongly indicated that the sluggish homogeneous equilibria $(ZnL_3\leftrightarrow ZnL_2 \leftrightarrow ZnL + L)$ that led to appearance of the second wave interfered to some significant extent with the heterogeneous kinetics of the first wave above pH 6. Even though the curve–fitting operations appeared to have resolved the two waves in the pH range 6 to 7.5,
the parameters extracted were compromised by the slow homogeneous kinetics that interfered with the slow heterogeneous kinetics for the first wave.

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

It was evident also from the polarographic complex formation curves (Figure 5.41) that the data obtained from the irreversible wave above pH 9 could not be used in refinement operations. The set of $E_{1/2}$ values obtained with the Ružič–based curve-fitting procedure were clearly determined with high levels of uncertainties to be used in refinement operations. The observed $E_{1/2}$ obtained with the Cukrowski curve-fitting method (which were essentially the same as $E_{1/2}^{irr}$ determined from the Ružič–based curve–fitting) would obviously not be applicable in refinement operations since one could not combine the potentials from the quasi–reversible first wave observed below pH 6 and the potentials from the irreversible second wave observed above pH 9. The variation in electrochemical reversibility was too huge for any of the curve–
fitting models used here to extract useful sets of potentials for use in refinement of stability constants.

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. Experimental conditions as in Figure 5.41.

To gain some insight on the computed stability constants, the set of data ($I_d$ and $E_{1/2}$) extracted from the first wave up to pH 7.5 was refined using the software 3D–CFC (described in section 3.3.1 of Chapter 3) and the software ESTA for which virtual potentials generated from the polarographic data were employed (as described in section 3.4 of Chapter 3). In the pH range considered only the complexes ML and ML$_2$ were expected as shown in the species distribution diagram that was presented in Figure 5.36. A summary of the refinement operations is given in Table 5.9. Good statistical fit could be found for refinement of stability constants for ML and ML$_2$ as shown for the polarographic complex formation curves shown Figure 5.42. However, the computed value for Log $\beta_{ML_2}$ was too large compared to the expected value from GEP determined in this work or reliable literature [3]. This underpinned the deductions made here on the complications of sluggish homogeneous equilibria.
influencing the reduction processes observed for the first wave. It was gratifying that the \( \log \beta_{ML} \) computed was in good agreement with the GEP or literature data, indicating that enough experimental information was reliably established for computation of the \( \log \beta_{ML} \) value from the first wave (pH below 6) prior to the appearance of the interfering second wave.

It was interesting to note that other polarographic results from literature [21], which were conducted at fixed pH and varying ligand concentration also showed good agreement of the \( \log \beta_{ML} \) value but larger value for the \( \log \beta_{ML2} \) suggesting that the no attention was given to complications of slow homogeneous kinetics.

Due to complexity of the Zn(II)–Glycine–OH system, all the voltammetric data must be seen as preliminary result. Systems of this nature which involve sluggish homogeneous kinetics as well as slow heterogeneous kinetics require further fundamental studies and this was out of scope of this project.

### 5.2.5 The Effect of Addition of a Methyl Group to a Ligand

In the introductory section of this chapter (section 5.1) an overview on the selected metal–ligand systems studied in this work was given. It was mentioned that in the preliminary study of glycine and sarcosine with the metal ions Cd(II) and Pb(II) [2], a trend of \( \log \beta_{ML} \) for the metal ions Ni(II), Zn(II), Cu(II) (\( \log \beta \) from [3]), Cd(II) and Pb(II) (\( \log \beta \) from [2]) as a function of metal ion radius [5], indicated that addition of a methyl group to glycine (effectively producing sarcosine) led to smaller \( \log \beta_{ML} \) values for sarcosine. However, the trend was not considered conclusive as the \( \log \beta_{ML} \) values found in the preliminary study for Cd(II) and Pb(II) appeared too close to each other being within the experimental errors of the experimental data collected.
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 °C and ionic strength of 0.5 M in NaNO$_3$. DCP and VP data derived from the $E'_{1/2}$ and $I_d$ extracted from analysis of the first DC wave between pH 5 and 7.5.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Log $\beta$</th>
<th>OF/HF*</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ML</td>
<td>ML$_2$</td>
<td>ML$_3$</td>
<td>ML(OH)</td>
</tr>
<tr>
<td>DCP</td>
<td>4.74 ± 0.05</td>
<td>9.51 ± 0.02</td>
<td>11.39(fixed)$^{[a]}$</td>
<td>9.85 (fixed)$^{[a]}$</td>
</tr>
<tr>
<td>DCP</td>
<td>4.82 ± 0.02</td>
<td>9.08 (fixed)$^{[b]}$</td>
<td>11.39(fixed)$^{[a]}$</td>
<td>9.85 (fixed)$^{[a]}$</td>
</tr>
<tr>
<td>VP</td>
<td>4.93 ± 0.02</td>
<td>9.22 ± 0.01</td>
<td>11.39(fixed)$^{[a]}$</td>
<td>9.85 (fixed)$^{[a]}$</td>
</tr>
<tr>
<td>VP</td>
<td>4.91 ± 0.02</td>
<td>9.08 (fixed)$^{[b]}$</td>
<td>11.39(fixed)$^{[a]}$</td>
<td>9.85 (fixed)$^{[a]}$</td>
</tr>
<tr>
<td>GEP</td>
<td>4.831 ± 0.001</td>
<td>9.081 ± 0.004</td>
<td>11.39 ± 0.02</td>
<td>9.85 ± 0.04</td>
</tr>
<tr>
<td>Literature Data (GEP)</td>
<td>4.85 ± 0.04</td>
<td>9.07 ± 0.07</td>
<td>11.5 ± 0.1</td>
<td>9.69$^{[b]}$</td>
</tr>
<tr>
<td>Literature Data (DCP)$^{[c]}$</td>
<td>4.88 ± 0.15</td>
<td>9.60 ± 0.22</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* OF--Overall Fit in mV (DCP); HF--Hamiltonian R-Factor (VP and GEP)
[a] Log $\beta$ values from the final model obtained by GEP (Table 5.8)
[b] $\mu = 0.15$ M, 37 °C
[c] Log $\beta$ values evaluated using Schaap and McMasters method [23]; ligand titrations at various fixed pH values in the range 3–6; $\mu = 1.0$ M, NaClO$_4$ medium, 25 °C.
Figure 5.43 is a plot of the variation in Log $\beta_{\text{ML}}$ values for the metal ions Ni(II), Zn(II), Cu(II), Cd(II), and Pb(II) as a function of their metal ion radii. The values used to generate the plot are summarised in Table 5.10, whereby the Log $\beta_{\text{ML}}$ values for Cd(II) and Pb(II) are those found in this work (compiled from final models established in this work –see Tables 4.5, 5.3, 5.5, and 5.7). The Log $\beta_{\text{ML}}$ for the other metal ions were compiled from literature [3]. Indeed a clearer trend of Log $\beta_{\text{ML}}$ as a function of metal ion radius was observed such that the Log $\beta_{\text{ML}}$ values for glycine were significantly larger than those for sarcosine (Log $\beta_{\text{ML}}$ values for sarcosine and glycine for the metal ions considered differ by about 0.4 log units). This trend suggests that ML complexes of glycine are somewhat more stable than the ML complexes of sarcosine, whereby the methyl group of sarcosine is responsible for steric destabilisation of the metal–ligand complex which overrides the inductive effect of the methyl group. Typically, the opposite effect is seen with methyl group substitution in ligands such as iminodiacetic acid (IDA) and its methyl derivative, $N$–methyliminodiacetic acid (MIDA), with the latter forming the more stable complexes.
This suggests that in the case of IDA and MIDA the inductive effect of the methyl group overrides the steric effect (if it exists at all).

**Table 5.10** Stability constants (as $\log \beta_{ML}$) 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.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Radius [Å]</th>
<th>$\log \beta_{ML}$ Glycine</th>
<th>$\log \beta_{ML}$ Sarcosine</th>
<th>$\Delta \log \beta_{ML}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>0.57</td>
<td>8.10</td>
<td>7.75</td>
<td>0.35</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.68</td>
<td>5.63</td>
<td>5.24</td>
<td>0.39</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.74</td>
<td>4.85</td>
<td>4.31</td>
<td>0.54</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>0.95</td>
<td>4.23</td>
<td>3.82</td>
<td>0.41</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1.19</td>
<td>4.58</td>
<td>4.19</td>
<td>0.39</td>
</tr>
</tbody>
</table>

From the DC polarographic studies of Cd(II)–Glycine–OH, Cd(II)–Sarcosine–OH, Pb(II)–Glycine–OH, and Pb(II)–Sarcosine–OH systems it was noted that for the systems involving glycine the recorded polarograms exhibited essentially reversible electrode processes whereas for the corresponding systems involving sarcosine departures from electrochemical reversibility were observed. It seems that the methyl group of sarcosine not only plays a role in destabilisation of the metal–ligand complexes due to steric effects, but also contributes to slower heterogeneous kinetics at the electrode surface.
5.3 CONCLUSIONS

5.3.1 Applicability and Limitations of Curve–Fitting Models for Analysis of DC Polarograms

Three nonlinear curve–fitting methods were explored in this work for analysis of DC polarograms collected on studies of metal–ligand systems. The curve–fitting methods were summarised in Table 5.1. Based on the studies of various metal–ligand systems that were conducted in this work (the case studies that were presented in sections 5.2.1 to 5.2.4) and deductions proposed elsewhere in the literature, an overview on the applicability and limitations of the curve–fitting methods investigated is given in this section.

The Cukrowski curve–fitting method (Equation 3.33): In analysing DC polarograms by way of nonlinear curve–fitting in order to test for electrochemical reversibility (using the parameter \( \delta \)), the Cukrowski curve–fitting method was found to be very useful. In situations where it works, faster and more reliable analysis of DC polarograms compared to the traditional logarithmic analysis was found. With an appropriate function to account for background current, a DC polarogram can be fitted with using this method to extract the reversibility index parameter \( \delta \), which can vary between 0 and 1. Polarograms that generate \( \delta \) values above 0.9 could be regarded as reversible. The value of \( \delta \) between 0.65 and 0.9 show typical quasi–reversible characteristics; \( \delta \) values below 0.5 indicate fully-irreversible polarograms, in this case the equation used in the curve–fitting method is simply that describing an irreversible DC wave where \( \delta \) is essentially the same as the true transfer coefficient \( \alpha \) (section 3.5.2.2 in Chapter 3). When using this method to test for electrochemical reversibility, \( \delta \) values between 0.5 and 0.65 should be checked by a second method such as logarithmic analysis to ascertain whether one is dealing with a quasi-reversible or irreversible system.
The method works very well with reversible systems to extract $I_d$ and $E_{1/2}$ in a single nonlinear curve-fitting procedure performed on a DC polarogram. It is also applicable in extracting $I_d$ and $E_{1/2}$ that can be used in refinement of stability constants by polarographic software based on computations of shifts in $E_{1/2}$ if the degree of electrochemical reversibility (regardless whether one is dealing with reversible, quasi-reversible, or irreversible systems) does not vary throughout the entire experiment, i.e. no variation in $\delta$ is observed for all polarograms considered in the entire range at which experimental data were acquired. The Cukrowski curve-fitting method has been used in a DCP study of fully-irreversible Ni(II) with the ligand methylenediphosphonic acid [24], where there was no significant variation in the parameter $\delta$ throughout the experimental range at which polarograms were recorded ($\delta$ was $0.4 \pm 0.05$ and $\delta$ was essentially equal to $\alpha$ in this case). The irreversible $E_{1/2}$ and $I_d$ extracted from curve-fitting were used in refinement of stability constants using the software 3D-CFC. The polarographic results were found to be in very good agreement with GEP result also conducted in the same study. For systems that exhibit significant variation in $\delta$, then the set of $E_{1/2}$ obtained from curve-fitting would not be applicable for use in modelling and computations of stability constants and in such cases the use of other fitting strategies to extract $E'_{1/2}$ should be considered. Two other curve-fitting methods were explored in this work to extract $I_d$ and $E'_{1/2}$.

*The Method based on Matsuda–Ayabe equation (Equation 3.44)*: This method was found to work well with reversible systems as well as a wide range of quasi-reversible systems to extract $I_d$ and $E'_{1/2}$, whereby from the test of electrochemical reversibility using the Cukrowski curve-fitting method, $\delta$ was in the range 0.65 to 1. In such cases, provided that an appropriate function is used to account for the background current, a single curve-fitting operation is usually sufficient to extract the reliable values of $I_d$ and $E'_{1/2}$. *This method was found unsuitable for irreversible systems.* If the degree of electrochemical reversibility changes significantly (from reversible to irreversible in the same set of experimental data) this method could not
predict $E'_{1/2}$ reliably from all recorded curves. When implemented in nonlinear curve–fitting, this method requires good initial guesses for the regression parameters. In cases where it worked, the method was found to be faster and more reliable in analysis of DC polarograms by computer–based curve–fitting to extract $E'_{1/2}$ compared to the traditional logarithmic analysis proposed by the original workers Matsuda and Ayabe who derived the theoretical equation that was adopted here for implementation in nonlinear curve–fitting of DC polarograms.

The method based on Ružić equation: This method was found to work equally well as the method based on Matsuda–Ayabe equation in cases of reversible and a wide range of quasi–reversible systems to extract $I_d$ and $E'_{1/2}$. For irreversible systems, it was found that the method based on Ružić equation would not give reliable estimates of $E'_{1/2}$, but the method gives reliable estimates of the irreversible half–wave potential $E^{irr}_{1/2}$, which are essentially the same as the observed $E_{1/2}$ obtained from the Cukrowski method. This implies that the Ružić–based curve–fitting method can be applied to extract $I_d$ and $E^{irr}_{1/2}$ from irreversible DC waves whereby the degree of electrochemical irreversibility does not change significantly in the entire range at which experimental data were collected, i.e., if $\delta$ obtained with the Cukrowski method (which is the same as $\alpha$ for irreversible polarograms) is regarded as constant, then the $I_d$ and $E^{irr}_{1/2}$ obtained can be used in refinement of stability constants based on shifts in half–wave potentials. Limitations of this method are encountered when the degree of electrochemical reversibility changes significantly (say from reversible to irreversible in the same set of experimental data) and one cannot use it to extract $E'_{1/2}$ from all recorded curves. The Ružić–based curve–fitting method has two half–wave potentials ($E'_{1/2}$ and $E^{irr}_{1/2}$). For this reason, it was found to be the preferred method to employ when dealing with non–reversible systems since in instances of reversible or quasi–reversible systems the $E'_{1/2}$ can be used in refinement operations, whereas in case of irreversible systems the $E^{irr}_{1/2}$ can be used too.
The applicability of the Ružič–based or Cukrowski curve–fitting methods to fully–irreversible systems to extract $I_d$ and $E_{irr}^{1/2}$ for use in computation of stability constants, where $\delta = \alpha < 0.5$ but $\delta$ (or $\alpha$) varies significantly (say by more than $\pm 0.1$ units), has not been checked. Such a system was not explored in this work.

One would think that the Ružič (or Matsuda–Ayabe) equations provided the answer for estimation of reversible potentials from analysis of non–reversible polarograms. The equations developed had a range of applicability and some limitations. All of the methods used take into account electrochemical reversibility phenomena due to slow heterogeneous kinetics (of diffusion–controlled processes) and complications from homogeneous kinetics or interfering processes at the electrode surface such as adsorption render these models practically useless.

5.3.2 Recommended Procedures in Analysis of DC Polarograms Recorded on Metal–Ligand Systems

Some useful equations were identified and tested for their applications and limitations in nonlinear curve–fitting procedures performed on DC polarograms collected on metal–ligand systems with reversible and non–reversible electrode reactions. The following is a summary of the recommendations made as output from the investigations performed in this work and those noted elsewhere, as far as analysis of DC polarographic data collected on metal–ligand systems is concerned, whereby such data are to be analysed to model the system and compute reliable stability constants:

- The first step in the recommended procedure is to ascertain the degree of electrochemical reversibility exhibited by all the recorded polarograms as a function of solution composition using a rather simple curve–fitting operation proposed by Cukrowski (Equation 3.33). Armed with a suitable nonlinear curve–fitting computer program, one would choose an appropriate background current function and use the Cukrowski curve–fitting method (Equation 3.33) to fit all the experimental polarograms to extract the reversibility index parameter $\delta$, $I_d$, and $E_{1/2}$. 234
The second step recommended is to perform analysis of variation in the parameter $\delta$ versus the experimental variable for solution composition (e.g. pH or $\log[L]$).

- If $1 > \delta > 0.9$ for all the experimental polarograms recorded, the set of $I_d$ and $E_{1/2}$ obtained can be used directly in modelling and refinement of stability constants (the $E_{1/2}$ values obtained in such a case can be regarded as essentially reversible half-wave potentials $E'_{1/2}$).

- If $\delta$ does not vary for all recorded polarograms at various solution compositions, i.e., the degree of electrochemical reversibility (or irreversibility) does not change ($\delta = \text{constant} \pm 0.05$), the set of $I_d$ and $E_{1/2}$ values obtained can be used directly in modelling and refinement of stability constants by using the software $3D-CFC$, which refines stability constants based on corrected shifts in half-wave potentials observed from a polarographic experiment.

- If $\delta < 0.5$ (fully irreversible systems), then observed $E_{1/2}$ obtained with the Cukrowski method is equal to $E^{ir}_{1/2}$ and $\delta = a$. One can use $E^{ir'}_{1/2}$ in refinement of stability constants.

- If fitting of the recorded polarograms using the Cukrowski curve–fitting method reveal variation in $\delta$ from some initial value above 0.9 to values below 0.9 (up to $\delta$ around 0.65), i.e., there is variation in electrochemical reversibility from reversible to quasi–reversible, then the $I_d$ and observed $E_{1/2}$ obtained with this curve–fitting method cannot be used in modelling and refinement of stability constants. In such a case, one should adopt either the method based on Matsuda–Ayabe equation (Equation 3.44) or the method based on the Ružić equation (Equation 3.49) together with an appropriate function to account for the background current to fit the experimental curves and extract $I_d$ and $E'_{1/2}$ for use in subsequent modelling and refinement operations.

- If, from using the Cukrowski curve–fitting method, a significant variation in $\delta$ is observed (say from reversible to irreversible) then one can only use the
Ružić method to extract $I_d$ and $E'_{1/2}$ from analysis of the reversible and quasi-reversible DC waves and only this set of data can be used for modelling and refinement operations. The data from irreversible waves would then not be considered in refinement operations.
5.4 REFERENCES