CHAPTER 1

INTRODUCTION

1.1 METAL–LIGAND EQUILIBRIA: GENERAL BACKGROUND

Whenever a metal ion is present in an aqueous solution, it interacts with other species (molecules or ions) present. Some of the interactions may form new species, called complexes, in which the metal ion is more or less strongly bound to other molecules or ions, namely the ligands. These interactions always lead to equilibrium situations when enough time elapses for equilibrium to be established. Such metal–ligand equilibria play substantial roles in analytical, organic and many other branches of chemistry, especially bio–organic and bio–inorganic and their knowledge is substantial to understand chemical processes involved. In particular, metal–ligand systems find many applications, ranging from nature to industrial processes, medicine to pollution control. The knowledge of the nature and concentration of particular species present in solution is required in such applications [1–4].

We may be concerned with problems such as the increased leaching of heavy metals from soils due to acid rain, the return to man of high level radioactive waste eluted by ground waters from its deeply buried container, or the distribution of particular biomedically–important metal–ligand complexes in blood plasma. Unfortunately, the total concentration of a species is seldom a measure of its bioavailability. Rather, knowledge of whether an element is likely to form species that are in appropriate forms, either to be transported from one system to another or to take part in processes within systems, is required. The studies of speciation (meaning the existence of the individual physicochemical forms of an element which make up its total concentration) are therefore becoming increasingly important [5].

In any attempt to understand chemical behaviour of systems in solution, whereby an assumption is made that there is equilibrium between the various chemical entities comprising the given system, knowledge of equilibrium constants is crucial. The equilibrium constant involving the formation of a metal complex from the aquo–metal ion and the most basic form of the ligand is a standard measure of the effectiveness of the ligand in coordinating metal ions. The constants involved are called stability constants or formation constants. Once the stability constants have been established, in principle, one can calculate models of equilibrium concentrations of species involved in the system of interest. The information obtained can be used to interpret many aspects of the behavior of a solution, e.g. what complexes are formed and under which conditions. The evaluation of stability constants, and hence determination of the composition of a given solution, is the basis of solution chemistry (or speciation) [1–2].

Three important, far–reaching developments have occurred recently in solution coordination chemistry which provides a major role for stability constant determinations and related information in the further development of the field. These new advances are: (i) the development of the chemistry of macrocyclic and macrobicyclic complexes, with the accompanying new challenges to ligand design and synthesis, and potential achievements in the study of new complexes with novel properties, high stabilities and important applications; (ii) the development of the new fields of bioinorganic chemistry and inorganic environmental chemistry, both of which require knowledge of the complexes formed in multicomponent systems containing many ligands and metal ions; and (iii) the development of computational methods for processing equilibrium data to provide more accurate and more rapid determination of stability constants, and the extension of the method to multidentate ligands, and to systems of many metal ions and ligands, that are too complex to have been investigated previously by classical methods. Now stability constants may be used, with the aid of appropriate computer programs, for the elucidation of the molecular and ionic species present in very complex biological and environmental systems [6–7].

In view of the increasing need to understand the interactions between ions in diverse mixed electrolytes, investigators in almost all fields of science require reliable stability constants for their systems and conditions [2].

1.2 GENERAL CONCEPTS IN EQUILIBRIUM ANALYSIS

A general equilibrium reaction involving chemical species A, B, C, and D is shown in Equation 1.1.

$$aA + bB \leftrightarrow cC + dD \qquad \textbf{(1.1)}$$

The equilibrium constant is nearly always determined as "concentration" constant, K_{eq}, in accordance with Equation 1.2, rather than as the so–called "thermodynamic" constant K^{th} indicated in Equation 1.3:

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \textbf{(1.2)}$$

$$K^{th} = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{([C]\gamma_C)^c ([D]\gamma_D)^d}{([A]\gamma_A)^a ([B]\gamma_B)^b} = K_{eq} \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \qquad \textbf{(1.3)}$$

where [i] is the molar equilibrium concentration of species i, a_i is the activity of species i and γ_i is the corresponding activity coefficient.

The main reason for this practice of determining concentration constants is the avoidance of the considerable difficulty, bordering on impossibility, of determining activity coefficients of complex charged species in solution. When the quotient of the activity coefficients is kept relatively constant by means of a large excess of an "inert" supporting electrolyte, the concentrations then parallel the activities over a wide range of concentration, when other interferences are avoided [2]. It has been pointed out that the values of the concentration constants are very close to the values of true thermodynamic constants for the ionic medium employed [8].

Some examples of the types of equilibria (in aqueous solutions) that may be involved in the formation of metal complexes, from a metal ion (M), a ligand (L), hydrogen (H) and hydroxide ions (OH), are presented below (in the equilibrium reactions charges are omitted for clarity):

1. Protonation of the ligand L

$$H + L \leftrightarrow HL \qquad K_1^H = \frac{[HL]}{[H][L]} \qquad \textbf{(1.4)}$$

or

$$H + L \leftrightarrow HL \qquad \beta_1^H = \frac{[HL]}{[H][L]} \qquad \textbf{(1.5)}$$

In general,

$$H + H_{r-1}L \leftrightarrow H_rL \qquad K_r^H = \frac{[H_rL]}{[H][H_{r-1}L]} \qquad \textbf{(1.6)}$$

or

$$rH + L \leftrightarrow H_rL \qquad \beta_r^H = \frac{[H_rL]}{[H]^r[L]} \qquad \textbf{(1.7)}$$

where K_r^H is a stepwise protonation constant for the *r*th protonation step and β_r^H is an overall protonation constant.

2. Formation of metal complexes with one metal centre

$$M + L \leftrightarrow ML \qquad \beta_{ML} = \frac{[ML]}{[M][L]} \qquad \textbf{(1.8)}$$

$$M + 2L \leftrightarrow ML_2 \qquad \beta_{ML_2} = \frac{[ML_2]}{[M][L]^2} \qquad \textbf{(1.9)}$$

In general,

$$M + qL \leftrightarrow ML_q \qquad \beta_{MLq} = \frac{[ML_q]}{[M][L]^q} \qquad \textbf{(1.10)}$$

3. Formation of polynuclear complexes

$$2M + L \leftrightarrow M_2L \qquad \beta_{M_2L} = \frac{[M_2L]}{[M]^2[L]} \qquad \textbf{(1.11)}$$

In general,

$pM + qL \leftrightarrow M_pL_q$ $\qquad \beta_{M_pL_q} = \frac{[M_pL_q]}{[M]^p[L]^q}$ **(1.12)**

4. Formation of complexes with protonated forms of the ligand

$M + H + L \leftrightarrow MHL$ $\qquad \beta_{MHL} = \frac{[MHL]}{[M][L][H]}$ **(1.13)**

In general,

$pM + rH + qL \leftrightarrow M_pH_rL_q$ $\qquad \beta_{M_pH_rL_q} = \frac{[M_pH_rL_q]}{[M]^p[H]^r[L]^q}$ **(1.14)**

5. Formation of hydroxyl complexes

$M + OH + L \leftrightarrow ML(OH)$ $\qquad \beta_{MLOH} = \frac{[ML(OH)]}{[M][L][OH]}$ **(1.15)**

In general,

$pM + yOH + qL \leftrightarrow M_pL_q(OH)_y$ $\qquad \beta_{M_pL_qOH_y} = \frac{[M_pL_q(OH)_y]}{[M]^p[L]^q[OH]^y}$ **(1.16)**

6. Hydrolysis of the metal ion M

$M + OH \leftrightarrow M(OH)$ $\qquad \beta_{MOH} = \frac{[M(OH])}{[M][OH]}$ **(1.17)**

In general,

$pM + yOH \leftrightarrow M_p(OH)_y$ $\qquad \beta_{M_pOH_y} = \frac{[M_p(OH)_y]}{[M]^p[OH]^y}$ **(1.18)**

In Equations 1.8 to 1.18 β_i represent the overall stability constant for the formation of complexed species *i*.

A general methodology used for elucidation of an equilibrium model, from a given set of experimental data obtained using a specific technique, is presented in Figure 1.1.

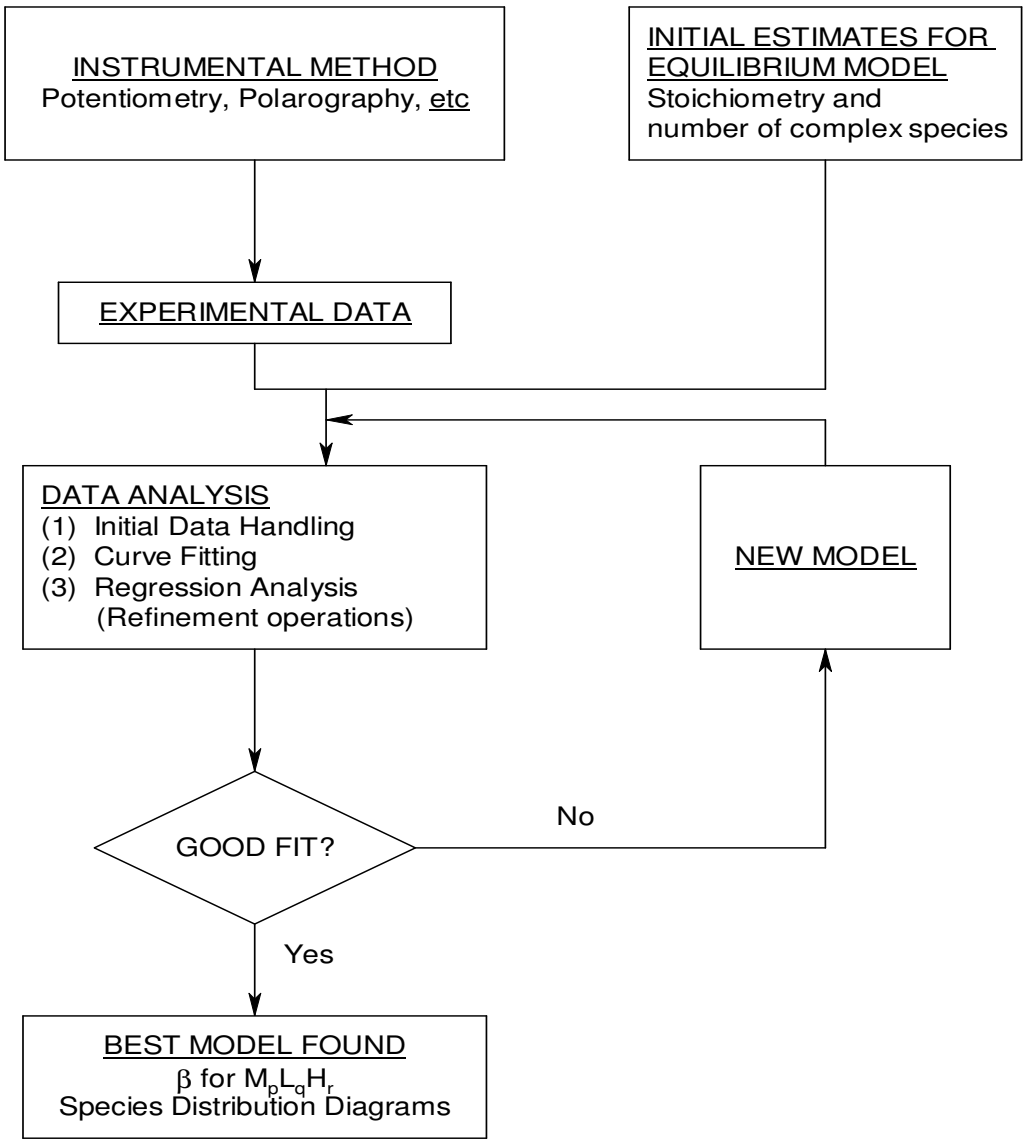

Figure 1.1: An overall scheme for equilibrium model determination (adopted from Legett et al. [7]).

Different aims are pursued in an equilibrium investigation. In general, the following aims are typically pursued [3]:

a) a proper model from analysis of the experimental data has to be found. The equilibrium model should define the number and stoichiometry of complexes formed during the experiment (in this regard one would consider all possible equilibria, such as those in Equations 1.4 to 1.18);
b) the corresponding stability constants have to be computed;
c) if possible, the structures of complexes identified have to be determined.

Indeed, any investigation of a metal–ligand equilibria system begins with a good choice of appropriate instrumental method(s) to be used to study the system of interest with as high accuracy, reproducibility and efficiency as possible. Then, appropriate computational techniques are chosen for interpretation of the experimental data with the final aim of establishing the stability constants for the most plausible metal–ligand model.

1.3 EXPERIMENTAL TECHNIQUES FOR METAL–LIGAND EQUILIBRIA STUDIES

Any analytical technique which may be used to determine with reasonable accuracy the concentration of at least one of the species in equilibrium, in which a metal complex is formed, can be used to study metal–ligand equilibria. The concentration of the monitored species together with the stoichiometry of the solution provides the information needed to calculate the concentrations of all of the remaining species present at equilibrium. If sufficient numbers of such equilibrium measurements are made over a range of experimental conditions (in which the concentrations of the species formed vary considerably) then accurate values of stability constants (that apply within the range of reaction conditions employed) can be obtained [1–2].

1.3.1 General Survey

In Table 1.1 a partial list of the methods available for measuring equilibrium constants of complex equilibria is presented. Spectroscopic and electrochemical methods are the most applicable and widely used in this regard. Even though many techniques can be used to study metal–ligand interactions in solution, one should bear in mind the fact that each technique has its limitations and advantages; and the generally accepted methodology in speciation studies of metal–ligand systems is to study a system of interest by more than one technique [1–2, 9].

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

Standard methods
• Potentiometry • Spectrophotometry • Specific metal ion electrodes (ion–selective electrodes, metallic and amalgam electrodes) • Nuclear magnetic resonance spectroscopy • Polarography • Ion–exchange • Colorimetry • Ionic Conductivity • Reaction kinetics • Partial pressure measurements • Solubility measurements
Competition Methods for Strong Complexes
• Ligand–Ligand competition measured potentiometrically • Metal–metal competition measured spectrophotometrically • Metal–metal competition by polarography • Ligand–ligand competition measured spectrophotometrically

Potentiometry[1] accounts for approximately 80% of the stability constants for various metal–ligand equilibria studies reported in the literature [1]. Potentiometry is generally supplemented or assisted by spectrophotometry[2] under special conditions. Spectrophotometric methods are, in general, highly sensitive, and as such are suitable for studying chemical equilibria. The limiting requirement in spectrophotometry is that the components involved in the chemical equilibrium must have distinct spectral responses, i.e., the species involved must absorb light. If this requirement is met the concentrations of the components involved in the equilibrium can be measured directly, and the determination of equilibrium constants is trivial. However, in many cases, the spectral responses of two and

[1] Potentiometry is the field of electroanalytical chemistry in which potential is measured under conditions of no current flow. In potentiometry, an electrode responding to one of the species in solution is used to measure its activity or concentration, depending on experimental conditions [10].
[2] Spectrophotometry is any technique that uses light to measure chemical concentrations [10].

sometimes even more components overlap considerably, and analysis is no longer straightforward [9].

Another method that has been employed to a considerable extent, and which may be further developed, involves the use of specific metal ion electrodes (or ion selective electrodes).

Glass electrode potentiometry, spectrophotometry, and specific metal ion electrodes combined form the basis of approximately 95% of all the stability constants reported in the literature [1]. These techniques, however, have a number of serious limitations that make it necessary to look for other experimental techniques, either as complimentary techniques that are used in aiding the modelling and optimization operations, or as full substitutes. Voltammetry[3], particularly polarographic techniques (where a drop of mercury is used as the working electrode), is used less often, but holds several advantages and can provide results inaccessible by other means [11–18].

1.4 POTENTIOMETRY

1.4.1 Basic Principles of Potentiometry

In potentiometry, information on the composition of a sample is obtained through the potential appearing between two electrodes. The equipment required for direct potentiometric measurements includes an ion–selective electrode (ISE) that acts as the indicator electrode, a reference electrode, and a potential–measuring device (a pH/millivolt meter that can read 0.2 mV or better). The indicator electrode is capable of selectively measuring the activity of a particular ionic species in the sample solution. Ion–selective electrodes are mainly membrane–based devices, consisting of permeable ion–conducting materials, which separate the sample from the inside of the electrode. The membrane is usually nonporous, water

[3] Voltammetry refers to techniques in which the relationship between voltage (or potential) and current is observed during electrochemical processes [10].

insoluble, and mechanically stable. The composition of the membrane is designed to yield a potential that is primarily due to the ion of interest (via selective binding processes, e.g., ion exchange, which occur at the membrane–solution interface) [19].

According to the Nernst equation, there is a direct relationship between the potential of the ISE and the logarithm of the activity or concentration of a species *A* being monitored by the ISE [19]. The overall relationship is given by Equation 1.19.

$$\begin{aligned} E &= E_k + E_j + (RT/nF)\ln a_A \\ &= E_k + E_j + (RT/nF)\ln[A] + (RT/nF)\ln y_A \end{aligned} \qquad \textbf{(1.19)}$$

where E is the total potential developed between the ISE and the reference electrode; E_k is a constant which is characteristic of the particular ISE; E_j is the diffusion (or liquid junction) potential; R, T, and F have their usual meaning; n is the number of electrons participating in the electrode reaction; y_A is activity coefficient of species A; a_A is the activity of species A; and $[A]$ is the concentration of species A (the molar concentration scale is assumed to be used).
A typical electrode commonly used in potentiometry is the glass electrode (GE), which selectively responds to the activity of hydrogen ions in solution. This type of potentiometry that uses glass electrodes is commonly known as Glass Electrode Potentiometry (GEP). In GEP, Equation 1.19 can be written as:

$$E = E_k + E_j + (2.303\,RT/nF)\log a_H = E_k + E_j + (2.303\,RT/nF)\text{pH} \qquad \textbf{(1.20)}$$

where $\text{pH} = -\log a_H$

The factor $2.303RT/nF$ is known as the slope of the GE and is determined by calibration of the GE, where potential differences of standard solutions of known pH are measured. Usually, the sum $(E_k + E_j)$ is regarded as a constant, provided E_j is maintained constant in the test solutions. In this way, the constant term $(E_k + E_j)$ is also determined as a single value from calibration results. Having calibrated the

glass electrode, one can measure directly concentration of hydrogen ions in sample solutions by simply recording the potential of the GE (measured against a reliable reference electrode) [6].

1.4.2 Potentiometry and the Study of Metal–Ligand Equilibria

Potentiometric measurements were first used for the measurement of stability constants by Arrhenius, Ostwald, and Nernst, who provided the basis for the introduction of electrodes responding reversibly and selectively to only one species present in solution [1]. The potentiometric measurement of stability constants is based primarily on the competition between hydrogen ions and metal ions for coordination sites on the ligand whereby metal complex formation involves displacement reactions of one or more protons from the ligand. Evaluation of stability constants usually involves solution of mass balance equations written for the total metal ion [M_T], ligand [L_T] and proton [H_T] concentrations. Refinement of stability constants, that involves the simultaneous solution of the above mass balance equations, is only possible if either the free metal ion [M], free ligand [L] or free proton [H] concentration, that can vary in a wide concentration range, can be monitored with high accuracy throughout an experiment [1–3].

The glass electrode is still the best potentiometric sensor with widest linearity range. It is then not surprising that glass electrode potentiometry became most powerful and most widely used analytical technique in the study of metal–ligand equilibria [1]. An additional and very important advantage of GEP is that the variation in free proton concentration always takes place when any kind of an organic ligand (that is involved in the protonation reactions) is investigated with any kind of a metal ion that is involved in the complex formation reaction with a protonated form of the ligand. The widely spread application of GEP also resulted in the development of powerful dedicated computer programs, such as SUPERQUAD [20], and ESTA [21–23], allowing analysis of a variety of metal–ligand systems. Moreover, potentiometry gained popularity in studies of metal–

ligand equilibria because the equipment required for performing potentiometric experiments is relatively inexpensive.

Unfortunately, potentiometry does have its limitations, as do most analytical methods. The accuracy of the potentiometric methods declines when the total concentrations of the components in the measured system diminish. In this regard, potentiometric sensors do not measure the concentration of free metal ions (or hydrogen ions in the case of glass electrode potentiometry) with sufficient accuracy. Furthermore, GEP is not reliable or accurate at the extremes of low and high pH (below 2 and above 12). The reason for this limitation is because of the fact that below pH 2 and above pH 12, hydrogen ions become extremely significant and responsible for greater conductance, thereby affecting liquid junction potentials. Also, several models can be found from analysis of potentiometric data and often difficulties arise in establishing the most plausible model [1–4, 24–25]. In these cases other methods such as spectrophotometry or polarography must be considered.

1.4.3 Computer–Assisted Experiments for Potentiometry

In recent years, computer–assisted experimentation has assumed a major role in the experimental laboratory, and computer–based systems are now being used widely by physical scientists [26]. Computers are supposed to make things easier, faster, or more automatic, that is, less work for the human host. Additional advantage of computer–assisted experiments is related to increased accuracy, reliability and reproducibility of experimental data. In general, instrumentation helps science and technology progress. Scientists and engineers around the world use instruments to observe, control, and understand the physical universe. It has been about half of a century since electronic digital computers were introduced. Even so, their use has seen enormous change and progress in the relatively brief span of years in which it has been possible to use computers. Most scientists are well aware of the enormous speed with which digital computers can carry out complicated calculations. This image of computers as essentially a computational

device has, for many, obscured another related and very important property of the digital computer. This is its capability to make very rapid control decisions or to communicate at high speeds with other types of devices, such as laboratory instruments. It is this feature that has found attraction in scientific and engineering fields whereby large amounts of experimental data are gathered from various experiments performed in such fields [27].

The introduction of digital computers into research laboratories has seen wide applications in automation of experimental data acquisition [28].The International Union of Pure and Applied Chemistry (IUPAC) defines automation as "the use of combinations of mechanical and instrumental devices to replace, refine, extend, or supplement human effort and facilities in the performance of a given process, in which at least one major operation is controlled without human intervention, by a feedback mechanism"[27].

Most experimental techniques used in studies of metal–ligand systems require collection of large amounts of experimental raw data. Hence, experiments performed manually are inherently labour–intensive and time–consuming. Moreover, such manual tasks are prone to human error and decreased reproducibility and accuracy of results obtained. Therefore, collection of accurate data of high quality requires highly skilled operators [6–7, 9]. Computer–based automated instrumentation is then highly desirable for collection of experimental data to ensure increased reproducibility, reliability and accuracy.

Basically, potentiometric experiments involve performing a titration, whereby, hydrogen and/or metal ion concentrations are measured by means of a suitable concentration probe(s), together with the volume of titrant added to produce that concentration. Conventionally, this could be performed by a manually operated microsyringe or microburette, research quality pH meter or electrometer, and a suitable titration vessel. Although this approach does lead, with suitable precautions, to precise data, it can be arduous to perform on a frequent basis, particularly if the potentiometric sensor used is slow to reach equilibrium.

The simplicity of equipment used for titrimetric experiments makes potentiometric experiments well suited for automation. Efforts in this area have been reported since 1947 [27], but not until the appearance of solid state electronics in the 1960's was the construction of a control unit for an automatic titrator made feasible.

Many automatic titrators have been constructed for the potentiometric study of complex formation and many descriptions can be found in the literature [27–32]. The early titrators were constructed from mechanical programmers and digital electronics [33–38]. They were mainly constructed for automated potentiometric titrations for analytical chemistry purposes, but stability constant studies could also be performed using those early titrators. The calculations to evaluate the stability constants were performed on main–frame computers off–line because of the complexity of the calculations. These titrators measured the potential of an electrode, mostly the glass electrode, a preset number of times and made additions of fixed volumes of titrant at fixed times.

More flexibility was offered by the introduction of computers [39–41] and microcomputers [42] into instrumentation for potentiometric complexation studies. For instance, these titrators tested the stability of the electrodes by estimating the drift between two consecutive measurements. This reduced the possible influence of slow electrode response or transient noise on the results.

For purely analytical purposes, titrators with end–point detection have been extensively developed. For example, a minicomputer [43] or a microcomputer [44–46] was incorporated to control the additions, acquire data, and calculate the end–point in acid–base potentiometric titrations. Some of these computerized equipment have been developed to perform virtually any kind of titration, e.g., potentiometric or spectrophotometric [45].

Automatic potentiometric titrations are widely used in industrial and research laboratories. Indeed there are currently many commercially–available automatic potentiometric titrators capable of performing various types of titrations, ranging

from simple acid–base titrations to titrations based on complex formation. Most modern automatic potentiometric titration systems are controlled via personal computers equipped with appropriate software [47– 48]. A major disadvantage with most of such equipment is that they cannot be easily modified. For example, in some research activities there maybe cases where additional measurements are required, together with the potentiometric data. In this regard the commercially–available potentiometric titrator may have many other useful features and versatility for potentiometric studies, but lack the flexibility to be modified to incorporate additional measurements of interest in research laboratories.

1.5 POLAROGRAPHY

1.5.1 Basic Principles of Polarography

Polarography is a type of voltammetric method. The original development of polarography was due to the 1959 chemistry Nobel laureate Jaroslav Heyrovský in the 1920's [49]. Voltammetry comprises a group of electrochemical methods in which information about the analyte is derived from the measurement of current as a function of applied potential. Unlike potentiometric measurements, which employ only two electrodes, voltammetric measurements typically utilize a three-electrode electrochemical cell. The use of the three electrodes (*working*, *auxiliary*, and *reference*) along with the potentiostat instrument (whose function is to observe the potential of the working electrode against the constant potential of the reference electrode) allows accurate application of potential functions and the measurement of the resultant current. The different voltammetric techniques that are used are distinguished from each other primarily by the potential function that is applied to the working electrode to drive the reaction, and by the material used as the working electrode [49–50].

Polarography is based on the unique characteristics of the current–potential curves obtained when solutions of electrooxidizable or electroreducible substances are electrolyzed in a cell in which one electrode (the working electrode) consists of

mercury falling drop-wise from a fine bore capillary glass tube (Dropping Mercury Electrode, DME). The detection limit depends on the technique used and can vary, for direct measurements, between 10^{-8} and 10^{-3} mol dm^{-3}.

Polarography is a voltammetric measurement whose response is determined by combined diffusion/convection mass transport. Polarography is a specific type of measurement that falls into the general category of linear–sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current versus potential response of a classical Direct Current (DC) polarographic experiment has the typical sigmoidal shape. The variation of current with a continuously changing potential is measured instrumentally to give a DC polarogram (or polarographic wave)[4].

In the presence of substances which undergo reduction or oxidation at a dropping mercury electrode, an increase in cathodic or anodic current is observed over a particular potential range of the polarogram. Subsequent to this potential range, a region is reached where the current is independent of potential and has a limiting value. The limiting current is typically diffusion–controlled (diffusion is the principal contribution to the flux of electroactive material at this point of the Hg drop life). The diffusion–controlled limiting current is called the *limiting diffusion current* (I_d). Most analytical applications of polarography are based on measurements of I_d because the value of I_d is related to the analyte concentration by the Ilković equation:

$$I_d = 708 n D^{1/2} m^{2/3} t^{1/6} C \qquad \textbf{(1.21)}$$

where D is the diffusion coefficient of the analyte in the medium (cm^2/s), n is the number of electrons transferred per mole of analyte, m is the mass flow rate of Hg through the capillary (mg/s), and t is the drop lifetime in seconds, and C is analyte concentration in mol. cm^{-3}.

[4] The graph of current versus applied potential in polarography is commonly called a polarogram or polarographic wave.

Another important parameter from polarographic waves is the half–wave potential ($E_{1/2}$), that is, the potential on a polarographic curve at which the current reaches half of its limiting value. Although the limiting current depends on concentration, $E_{1/2}$ is frequently almost independent of the concentration of electroactive species. For electrochemically reversible redox reactions, the value of $E_{1/2}$ is closely related to the standard redox potential $E°$, and in general, the $E_{1/2}$ is characteristic of the compound undergoing reduction or oxidation. Because $E_{1/2}$ depends on the nature of the electrolyzed substance and therefore the composition of the solution, etc., it is a quantity that can be used to reflect chemical effects, such as complexation of the electroactive substance [50–51].

Modified Voltammetric Methods

In the absence of an electroactive substance of interest, and between the anodic and cathodic background limits, a residual current (also referred to as background current) flows. The residual current is composed of a current due to double–layer charging (charging or capacitive current) and a current caused by low–level oxidation or reduction of trace impurities in the system. Quantitative classical polarography with DME is limited to solutions with concentrations greater than approximately 10^{-5} mol dm^{-3}. This limitation results from the non–faradaic current associated with the charging of each mercury drop as it forms. When the ratio of the faradaic current (current produced from reduction of analyte) to non–faradaic current approaches unity, large uncertainties in determining diffusion currents are observed. Modifications to the classical methods have been made in order to increase the ratio of faradaic to non–faradaic contributions, thus permitting the quantitative determination of species at much lower concentrations. Some of the modified techniques are Sampled Direct Current Polarography, Normal Pulse Polarography (NPP), and Differential Pulse Polarography (DPP) [51].

Sampled Direct Current Polarography

The modification of the classical DC polarographic technique involves measurement of current only for a short period near the end of a lifetime of the mercury drop. A mechanical knocker is used to detach the drop after a reproducible time interval. Because of this the method is called sampled direct current polarography or "TAST" polarography (German for touch). Instead of recording the current as a function of applied voltage on a continuous basis, the current is only sampled for a period of 5 to 20 ms just before the detachment of each drop. This enables the contribution of the charging current to the overall current to be minimized. Between sampling periods the recorder is maintained at its last current level by means of a sample and hold circuit.

The advantage of current sampling is that it reduces the large current fluctuations due to the continuous growth and fall of drops that occurs when using a DME. Since current near the end of a drop lifetime is nearly constant, a smooth curve is generated as a result of this with significantly smaller current fluctuations compared to classical DC polarography. This results in improved precision and detection limits. All theoretical current–potential relationships applicable for classical DC polarography also hold in the case of sampled DC polarography [51].

Figure 1.2 illustrates the principles of sampled DC polarography. A typical polarogram obtained from sampled DC polarographic measurements of a solution containing an electroactive metal ion is shown in Figure 1.3. The convention used for plotting polarograms in this dissertation has reduction (or cathodic) current as positive and a potential scale that is positive to the right and negative to the left.

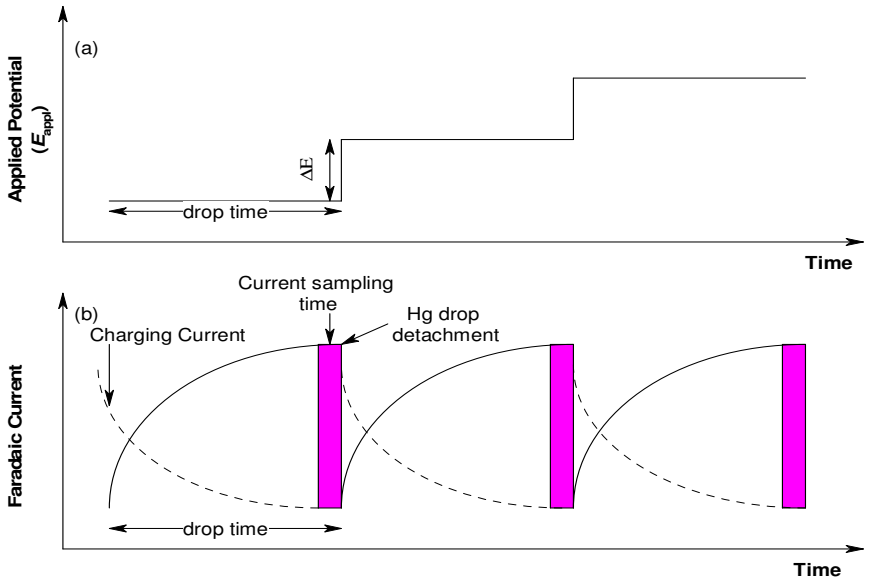

Figure 1.2: Sampled DC polarography. (a) Stepwise potential waveform. (b) Current–time curves observed in response to the potential steps and current sampling scheme. The experiment is a series of cycles in which a potential is established and held constant for a period, a current sample is taken toward the end of the drop lifetime, then the drop is dislodged and the potential is changed by an amount ΔE.

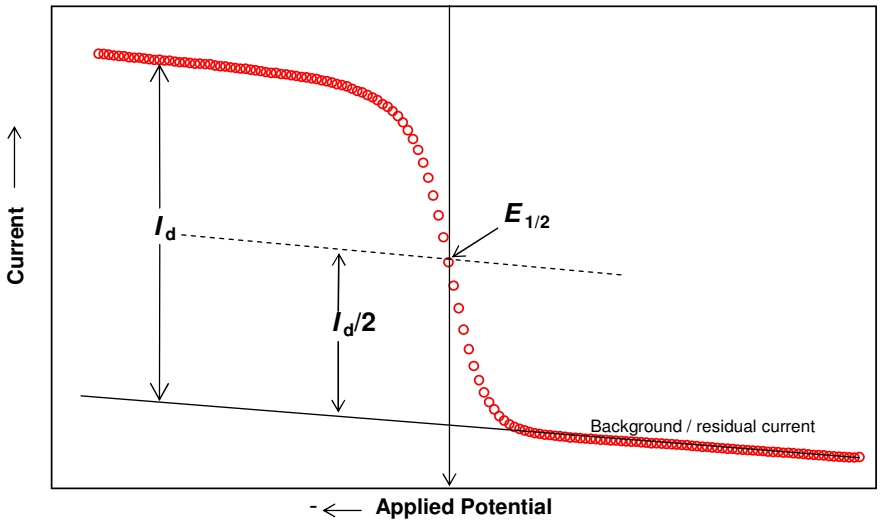

Figure 1.3: A typical sigmoidal–shaped sampled DC polarogram.

Pulse–based polarographic techniques

The two most common pulse techniques involve the normal and differential methods. A direct current voltage pulse is applied for a period of about 60 ms just before the mercury voltage drop is detached from the capillary by a mechanical knocker. In the case of normal pulse polarography (NPP) the size of successive pulses is increased linearly with time. The resulting current is then sampled for the last 5 to 20 ms of the drop.

In differential pulse polarography (DPP), a direct current pulse of between 20 to 100 mV is applied for about 60 ms just before the detachment of the mercury drop from the capillary. Two current measurements are made, one just prior to the direct current pulse and the other near the end of the pulse. The difference in currents is recorded as a function of the linearly increasing voltage. At the end of a scan, a differential curve results which consists of a peak that is directly proportional to the concentration of the analyte.

An advantage of the derivative type polarogram is that individual peak maxima can be observed for substances with half-wave potentials differing by as little as 0.05 V, in contrast to classical and normal techniques, which require a potential difference of at least 0.1 – 0.2 V for resolution. DPP has even better ability to discriminate against capacitive current because it measures a difference current (helping to subtract any residual capacitive current that remains prior to each step). Limits of detection with Differential Pulse Polarography are typically in the range 10^{-8} – 10^{-9} mol dm^{-3} [51].

1.5.2 Polarography and the study of Metal–Ligand Equilibria

As far as the study of solution equilibria is concerned, polarography has been infamous compared to glass electrode potentiometry. Reluctance to use polarography maybe related to the greater ease of generation of potentiometric data and its interpretation, particularly with the advent of computer programs that greatly facilitated analysis of the potentiometric data [1]. Widespread availability

of automated potentiometric instrumentation may also be a reason in the reluctance to use polarography for investigations of metal–ligand equilibria.

However, polarography constitutes a powerful and versatile technique for the study of complexes in solution and can have definite advantages, and sometimes can provide answers inaccessible by other means. The low detection limits of polarography (using a direct measurement at total metal ion concentration range between 10^{-3} and 10^{-8} mol dm^{-3}) makes it advantageous in situations of low complex solubility and when dealing with easily hydrolazable ions to form hydroxide precipitates. The ability of polarography to work at relatively low total metal ion concentrations means that precipitation of solid hydroxides will thermodynamically occur at much higher pH values. The consequence of this is that with polarographic experimental conditions more species are typically identified than in potentiometric experiments. Even more important, very acidic metal ions such as Bi^{3+} form complexes at very low pH which can usually only be studied by polarography [1, 13–16].

In addition, voltammetry (or polarography) provides a kind of spectrum that can be interpreted in terms of intensity and position of signals recorded. The position of the signal, the shift of the signal, and the intensity as well as the shape of the signals recorded on voltammetric spectrum provides also some insight into the nature of complexes formed [15, 18].

Polarography, as all other voltammetric techniques, is a dynamic and in principle non–equilibrium analytical technique; it does not allow a direct measurement of any of the free ion concentrations relevant in metal–ligand equilibria as is the case with potentiometric techniques. Polarographic measurements, however, result in a signal whereby the position (on the potential scale) and intensity (on the current scale) depend on solution composition.

The use of experimental polarographic data in mathematical models, in order to obtain stability constants, is based on two observations. The first is that half–wave

potential[5] (or peak potential in the case of pulse polarography such as DPP) is shifted almost invariably to the more negative directions of applied potential as the pH is increased (for protic ligands) or the ligand concentration is increased (for any ligand). Secondly, the diffusion current changes and usually becomes smaller [1, 11–18, 52]. This implies that studies of metal complexes, by means of polarography, involve the determination of shifts in half–wave potentials and diffusion currents (for Direct Current Polarography), or shifts in peak potential and peak current (for Pulse–based Polarography) of metal ions in the presence of a complexing ligand .

Early methodologies

Several methods were developed to study metal–ligand equilibria by polarography in the past seventy years. The first method was reported by Lingane [53]. Lingane derived an equation (Equation 1.22) describing a shift in half–wave potential as a function of the excess of a ligand at fixed pH, allowing an evaluation of a stability constant for a single complex ML_q present in a solution when a fully–labile[6] metal–ligand system and reversible electrochemical processes were observed.

$$\Delta E_{1/2} = (E_{1/2})_s - (E_{1/2})_c = \frac{RT}{nF} \ln \beta_{ML_q} + q \frac{RT}{nF} \ln[L] \qquad \textbf{(1.22)}$$

In Equation 1.22, $(E_{1/2})_s$ and $(E_{1/2})_c$ are the half-wave potentials of the free metal ion and the complexed metal ion respectively. [L] is the concentration of the free ligand, and q and β_{ML_q} are the coordination number and stability constant of the complex ML_q. R is the universal gas constant, T stands for temperature at which experimental data is collected, n is the number of electrons involved in the electrochemical process and F is the Faraday constant.

[5] Half–wave potential ($E_{1/2}$) is the potential at which current resulting from a polarographic electrochemical process is half that of the limiting diffusion current (I_d) for that process.
[6] In a labile system the free metal, the free ligand, and metal–ligand species present at the electrode surface are in rapid equilibrium relative to the timescale of the electrochemical technique employed to study the system.

DeFord and Hume [54–55] reported later equations that were derived on the same assumptions as those reported by Lingane. Their method had advantage over the method of Lingane in that it allows the calculation of formation constants for the metal–ligand system where several complexes are formed in a stepwise manner. Schaap and McMasters [56] developed a logical extension of the DeFord–Hume method by applying the latter cases where metal ions complex simultaneously with two ligand species in solution. These polarographic methods were worked out for polarographic experiments at fixed pH and varied excess of ligand concentration. Furthermore, the mentioned methods are best applicable to simple ligands, usually non–protic (ligands with no protons bound to donor atoms where metal ions can compete to occupy) or fully–deprotonated ligands such as OH^-. All of the methods mentioned above showed very limited field of applications as they were based on a simple data interpretation without involving mass balance equations.

Possibly the most significant contribution in establishing stability constants by polarography comes from the school of Schwarzenbach [57, 58] who derived a simple equation, based on measurement of diffusion currents, allowing analysis of systems involving two metal ions competing for a single ligand when fully inert (or nonlabile[7]) complexes were formed. Among many theories and methodologies described for instance in a book by Crow [52] there is not a single contribution that involves mass balance equations and a typical analytical procedure as performed in a glass electrode potentiometric experiments, e.g., acid–base titration.

The interaction of metal ions with polyelectrolytes has also been studied by polarography [59–66]. However, theoretical considerations were of such complexity that only simplified solutions could be arrived to. The analytical procedures employed as well as exclusion of mass balance equations lead to significantly restricted applications related mainly to the formation of ML_q complexes investigated by a ligand titration at fixed pH value.

[7] In nonlabile systems, the rate at which the ligand, metal ion, and complex species is in equilibrium is slower than the timescale of the polarographic reduction process [1].

Recent Methodologies

A relatively new methodology and theory of speciation by polarography was recently developed and tested on numerous metal–ligand systems that show a diverse polarographic behavior. Fully labile [12, 14, 16, 18], inert (nonlabile) [67, 68] or mixed [69] metal–ligand systems on the polarographic timescale were investigated under typical GEP analytical procedures, e.g., at fixed total ligand and total metal ion concentration ratios (L_T : M_T ratios) and varied pH (acid–base titrations). A single mathematical expression (Equation 1.23) and a concept of complex formation curves [14, 18] (experimental and theoretical) were used in modelling and refinement operations that involve simultaneous solution of mass balance equations for [M_T] and [L_T] allowing also a successful use of polarography in the study of polynuclear species [14].

$$E(M) - E(C)_{x(i)} - \frac{RT}{nF}\ln\left(\frac{I(C)}{I(M)}\right)_{x(i)} = \frac{RT}{nF}\ln\left(\frac{[M_T]}{[M]}\right)_{x(i)} \qquad \textbf{(1.23)}$$

In Equation 1.23 E(M) and E(C) stand for the potential (either half–wave potential $E_{1/2}$ in DC polarography or peak potential E_p in pulse–based polarography such as DPP) in the absence and presence of metal complexes, respectively; I(M) and I(C) stand for current (either limiting diffusion I_d or peak I_p current) in the absence and presence of metal complexes, respectively. $x(i)$ stands for pH(i) or [L_T](i) for the ith polarogram recorded during acid–base (at fixed L_T : M_T ratio) or ligand titration (at fixed pH), respectively, of a metal–ligand system under investigation; R, T, F and n have their usual meaning. This recent methodology outlined above will also be referred to as the *Cukrowski method of speciation*.

The Cukrowski method of speciation can be employed at fixed ligand to metal ion concentration ratio and varied pH, by carrying out titrations with a ligand at fixed pH, by carrying out titrations with a metal ion at fixed pH, or a combination of all the analytical methods stated [12, 14, 16, 18, 67–69]. Unlike the earlier polarographic methodologies, the Cukrowski method of speciation involves

refinement operations that include solving mass balance equations written for fully labile, nonlabile, or mixed metal–ligand systems with the requirement that the electrochemical processes observed are electrochemically reversible on the polarographic timescale employed. In summary, this recent method provides a powerful and versatile means of analyzing experimental speciation data by polarography. The expression can be used for any metal–ligand model, including polynuclear metal species, for any ligand to metal ratio and for more than one ligand competing in the complex formation reaction.

1.5.3 Reversibility of Electrode Reactions

Several critical factors have to be considered when studying metal–ligand systems by polarography (or voltammetry). These factors include the presence of side reactions, the association and dissociation rates of the complexes compared to the timescales of the measurements (which makes the complexes labile or inert), and electron–transfer kinetics at the electrode surface relative to the timescale of the measurements (which makes the electrochemical processes reversible or irreversible) [52].

In metal–ligand equilibria studies, it is necessary for electrochemical processes to take place almost totally reversibly if direct use of potential data is to be valid in the use of polarographic methods such as those proposed by Lingane [53], DeFord and Hume [54, 55] and Cukrowski [12, 14, 16, 18, 67–69]. Unfortunately, the majority of electrode reactions at the dropping mercury electrode are non–reversible, being classified as quasi–reversible or irreversible depending on the extent of departure from electrochemical reversibility [52, 70, 71]. In metal–ligand equilibria investigations, departure from electrochemical reversibility can be observed when different complexes are formed, say, as pH is varied or ligand concentration is changed. Therefore, for polarography to be a diverse and useful technique in speciation studies, it is important to have methodologies that can handle metal–ligand systems involving not only reversible reactions, but also those systems that exhibit deviations from reversibility.

An electrode process is described as reversible if the equilibrium between the oxidized and reduced forms is established so rapidly that the electrode potential can be described by Nernst equation and the current is controlled only by the rate of diffusion of the electroactive species to the dropping mercury electrode. Quasi–reversible processes are those in which the corresponding polarographic signals are controlled simultaneously by diffusion and by an electrochemical step whose backward rate is not negligible with respect to the forward one. An irreversible electrode process is controlled by diffusion and an electrochemical step whose backward rate is negligible with respect to the forward rate [71]. In practice, electrochemical reversibility is a relative concept which depends on the timescale of the electrochemical technique employed. Thus, a wave which is quasi–reversible in the timescale of normal pulse polarography, NPP (10 – 100 ms) may well be completely reversible in the timescale of DC polarography (0.5 – 5s) [72].

Unlike in other polarographic techniques, in DC polarography the limiting diffusion current I_d remains essentially the same regardless of the degree of electrochemical reversibility [52, 70, 71]. In DPP, for instance, departures from electrochemical reversibility lead to decrease in the peak height as well as the shift in the peak potential to more negative potentials [73]. Thus, any methodology that may be used for prediction of reversible peak potential must also, as accurately as possible, predict the peak height that would correspond to the reversible potential. The unique feature of DC polarography has made it to be the technique of choice in polarographic studies of metal complexes involving non–reversible electrode reactions, since for non–reversible polarograms the only problem to be solved is the estimation of the reversible half–wave potential $E_{1/2}^{r}$ [74].

There have been two main groups of methods devised for the determination of stability constants of metal complexes which undergo non–reversible reductions at the dropping mercury electrode. The one group of methods is based on measurement of diffusion currents and diffusion coefficients and the other is based on half–wave potential determination.

Kačena and Matoušek [75] developed a method that is applicable to either reversible or irreversible systems involving formation of a single complex. Their method is based upon measurement of the change in diffusion coefficient of a metal ion when it becomes complexed. Simple relationships between diffusion currents observed, diffusion coefficients measured, and stability constant, lead to evaluation of the stability constant of the single metal complex.

The methods based on measurements of diffusion coefficients have serious limitations since the required data are not always conveniently available. Furthermore, only simple complexes can be evaluated with such methods and their applications have not found widespread use in literature [52].

Bond [70] proposed that if in polarographic studies of metal complexes, where there is an insignificant change in the degree of electrochemical reversibility (over the entire ligand concentration range), then to a good approximation the observed half–wave potential $E_{1/2}$ is related to the reversible half–wave potential $E^r_{1/2}$ by

$$E_{1/2} = E^r_{1/2} + \text{Constant} \qquad \textbf{(1.24)}$$

Under these conditions, the measured shift in half–wave potentials $\Delta E_{1/2}$ would be the same as $\Delta E^r_{1/2}$ over the entire ligand concentration range. In other words, the observed half–wave potentials and the corresponding I_d values can be used directly for determination of stability constants. Bond tested his method in a study of Zn(II)–Fluoride system at fixed pH and varied ligand concentration and he successfully used the Lingane method for computation of the stability constant for the ZnF^+ complex [70]. However, it should be noted that Bond's method can be generalized to other polarographic methods that involve calculations of shifts in potentials (peak or half–wave) such as the De Ford–Hume method and the more robust Cukrowski speciation method.

Matsuda and Ayabe [76–79] developed a general case, for the reduction of complexes, involving both the reversible reduction of the complex and the non–

reversible reduction. Matsuda and Ayabe derived an equation describing the current–potential relationship of a DC wave corresponding to reduction of complex ions which is reversible, quasi–reversible, or totally irreversible. In the method of Matsuda and Ayabe, a logarithmic analysis of the current–potential data, for each recorded polarogram, lead to an approximation of the reversible half–wave potential in the case of reversible or quasi–reversible systems. For totally irreversible systems no prediction of the reversible half–wave potentials was possible, but their method allowed computation of stability constants when the transfer coefficient α was independent of ligand concentration at fixed pH.

Ružić and co–workers [80] derived another equation describing the current–potential relationship of DC polarograms. Ružić and his co–workers derived their equation from that of Matsuda and Ayabe [76–79]. In the Ružić's method, the equation derived is used in conjunction with a graphical method proposed by Koryta [81] to estimate reversible half–wave potentials from logarithmic analysis of quasi–reversible DC polarograms.

All of the methods that were developed for studying metal–ligand systems involving electrochemical processes deviating from electrochemical reversibility were tested, to date, for simple ligands and complex formation at fixed pH. Moreover, tedious graphical procedures, such as logarithmic analysis, had to be performed for analysis of the polarographic curves recorded. Such graphical methods are prone to errors. It should be noted that these methodologies were developed in an era when computers were just being introduced and simplistic polarographic methodologies for studies of metal complexes were mainly available.

As mentioned in the preceding section, the Cukrowski method of speciation can be carried out to study speciation of metal complexes at fixed ligand to metal ratios and varied pH; by carrying out titrations with a ligand at fixed pH; by carrying out titration with a metal ion at fixed pH; or a combination of all the methods stated. The refinement operations that are invoked to determine stability constants require the use of reversible half–wave potentials (when direct current

polarography is employed) and the I_d values for each recorded polarogram. If the reversibility of the electrochemical system under study does not vary much throughout the experiment, from free metal ion to most involved solution composition with several complexes, then as Bond [70] proposed the determination of the stability constants is relatively straightforward. If a particular metal–ligand system involves significant deviations from electrochemical reversibility, then to successfully use the Cukrowski's method of speciation (to determine stability constants of several species that may be formed), a good methodology is needed to take into account the deviations from reversibility.

1.5.4 Computer–Assisted Experiments for Polarography

To understand the advantages of microprocessor applications in polarography (voltammetry) it is essential to recognize that the instrumentation required is far simpler when implemented digitally rather than by an analog approach. In polarography, signals consisting of combinations of the variables such as current (*I*), potential (*E*), and time (*t*), are applied to an electrochemical cell via a potentiostat[8] or galvanostat[9] and responses (usually represented as *I–E*, *I–t*, *E–t* curves) may be obtained from the electrochemical cell. The point to be emphasized is that the entire requirements in this branch of science are simply a function generator (used to produce the desired electrical signals or waveforms to be applied to the electrochemical cell), potentiostat, electrochemical cell (including electrodes) and a data acquisition system [50, 51].

Virtually all polarographic techniques are now carried out with the aid of a dedicated computer. Advances in electrochemical instrumentation closely followed the state of the art in electronic components, and the use of digital circuitry to perform many functions previously undertaken in the analog format [82]. Most electrochemical instrumentation now utilize a microprocessor for signal generation and data acquisition, and a personal computer for interaction with the operator, overall experimental management, and analysis and display of

[8] A potentiostat is an electronic device used for enforcing a controlled potential at an electrode.
[9] A galvanostat is an electronic device used for controlling current through an electrochemical cell.

results [51]. Many advantages have been derived in the field of electrochemical instrumentation due to introduction of computers. For example, computers have added versatility for generating complex waveforms used in electrochemical techniques such differential pulse polarography [83]. Computers have also simplified the control of timing of different phases of experiments in polarographic (voltammetric) experiments (e.g., dearation of solutions, stirring, and growth of a mercury drop) [84].

As for potentiometric titrators, polarographic analysers are well suited for automation, to some extent, depending on the nature of application of the polarographic methods.

Voltammetric experiments using commercially available instruments are mainly computerized, rather than automated [27, 85] due to the extensive use of voltammetry in analytical chemistry. A computerized experiment or process relies heavily on the human operators – the computer simplifies some tasks by taking some measurements but it's far from being a hands–off process. An automated experiment, on the other hand, is one where you set up the equipment, press the Start button on the computer screen, and watch while the computer orchestrates a sequence of events, takes measurements, and presents the results. Some examples of automated voltammetric instruments designed for applications in analytical laboratories, whereby samples are analyzed in repetitive procedures, can be found in the literature [86, 87]. Several commercially–made semi–automatic voltammetric instruments are also available [47, 48].

In polarographic studies of metal–ligand equilibria, either a sample solution containing a specific concentration of a metal ion is titrated with a ligand solution at fixed pH or a solution of fixed L_T : M_T ratio is titrated with a base or acid to vary pH. Polarograms are recorded at various pH values or ligand concentrations. Typically, the variation in solution composition (variation in pH or ligand concentration) has been achieved by manual titrant additions and polarograms recorded with the aid of a computer [88, 89]. In this regard, polarographic experiments involving metal–ligand equilibria have mainly been computerized

rather than automated. Inherently, the titrations performed in polarographic experiments of metal–ligand systems carried out as outlined above can be highly tedious and probably have resulted in polarography being used less often compared to potentiometry in studies of metal–ligand systems.

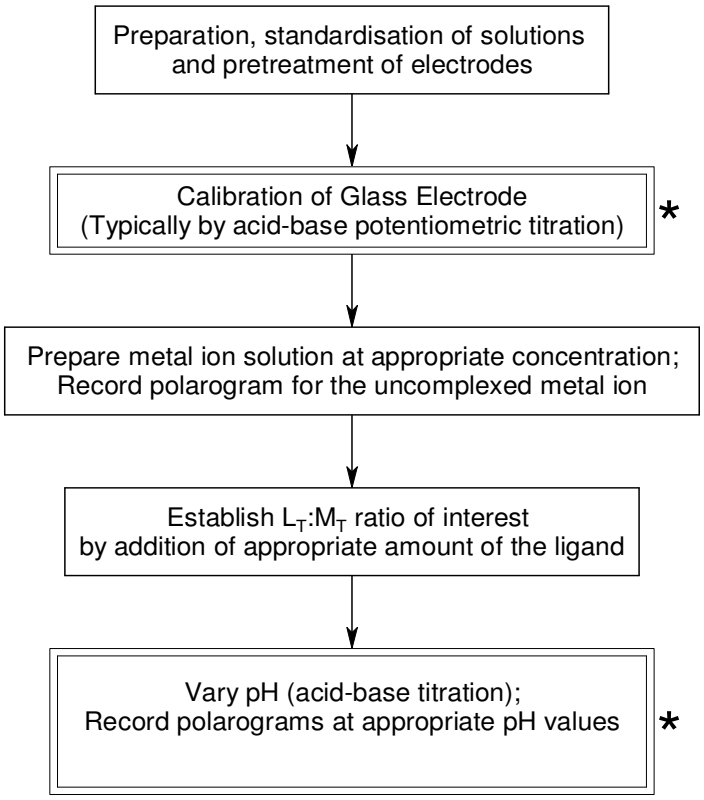

Figure 1.4: A flowchart depicting experimental tasks typically performed in a polarographic study of a metal–ligand system at fixed L_T : M_T and variable pH. The highlighted experimental tasks (*) are titrations which could be fully–automated.

The most important polarographic method, from the point of view of pH–dependent formation of metal–ligand species, is analyzing polarographic data collected at fixed ligand to metal concentration ratios and variable pH (the Cukrowski speciation method). Since the Cukrowski method of speciation involves refinement operations that involve solving mass balance equations, as many as possible experimental points should be collected and fed into the refinement procedures (if accurate stability constants have to be determined). A flow chart showing the experimental tasks to be performed in such experiments is

shown in Figure 1.4. In this regard, a computer–controlled instrumental set–up, that is capable of automated potentiometric and polarographic measurements, is advantageous in carrying out the necessarily tedious titrations.

Another advantage of using an automated instrumental set–up is the superiority over manual methods with respect to reproducibility, reliability and accuracy. Furthermore, information obtained by using an automated instrumentation is usually not conveniently obtained at the desired frequency by manual methods.

Unfortunately, there are no commercial instruments that can allow simultaneous polarographic and potentiometric data acquisition on one solution sample whereby the solution composition is varied systematically by a titration, e.g., for applications in metal–ligand studies at fixed L_T : M_T ratio and varied pH.

1.6 AIMS AND SCOPE OF PROJECT

The specific aims and objectives of this project were:

- To develop a dedicated, computer–controlled instrumental set–up, capable of automated polarographic and potentiometric measurements, either simultaneously on one solution sample or as independent techniques on different solution samples, with particular application to the study of metal–ligand systems by potentiometry and/or polarography at fixed total ligand and total metal ion concentration ratios with variation in pH.

- To develop methodologies, for implementation in computer–based curve–fitting operations, to allow evaluation of reversible half–wave potentials from metal–ligand systems that deviate from electrochemical reversibility. Such metal–ligand systems would be studied by Sampled Direct Current Polarography (DCP) and the methodologies would be derived from appropriate equations identified from literature.

- To verify the envisaged methodologies, for evaluation of reversible half–wave potentials, as applied to polarographic data for determination of stability constants, by using the well–established speciation technique of Glass Electrode Potentiometry (GEP).

The polarographic and potentiometric instrumental set–up developed in this project would be restricted to Sampled Direct Current Polarography, the most basic and widely applicable polarographic technique for solution chemistry studies, and glass electrode potentiometry, the most widely applicable potentiometric method in metal–ligand equilibria studies. However, the overall instrumentation would be such that easy modifications performed on it would lead to incorporation of more polarographic and/or potentiometric techniques. The overall instrumental set–up would be achieved by interfacing appropriate commercially–available and custom–built hardware components to a personal computer equipped with software for overall control of the automated experiments. Furthermore, the automation process would be restricted to the experimental tasks involving tedious titrations. The less tedious tasks such as transfer of samples, sample changing etc would be conducted manually. The automated instrumentation would ensure less tedious and more reproducible experiments and increased versatility in polarographic experiments of metal–ligand equilibria systems.

Validation of the instrumentation would be conducted by studying well–known metal–ligand systems to confirm reproducibility and reliability of results obtained.

The use of the envisaged computer–based nonlinear curve–fitting operations for analysis of non–reversible DC polarograms should be more versatile and advantageous than the traditional graphical methods used in literature. The appropriate models derived from literature, for adaptation in nonlinear curve–fitting operations, would be tested on selected metal–ligand systems that had been studied independently elsewhere and involve deviation from electrochemical reversibility when studied by DC polarography (in this case at fixed L_T : M_T ratio and varied pH). Furthermore, the validity of the curve–fitting operations,

performed on the DC polarographic data of the selected metal–ligand systems, was checked by performing GEP experiments of the said metal–ligand systems and comparing the stability constants obtained with those obtained from refinement operations of the DC polarographic data.

1.7 SUMMARY OF CHAPTERS

This dissertation contains six chapters including the current chapter (Chapter 1). In this chapter the relevant literature review on metal–ligand equilibria studies was given with particular emphasis on the potentiometric and polarographic methods. Furthermore, the overall objectives and scope of this research project were provided.

In Chapter 2, general descriptions of the materials, instrumentation, electrodes, and experimental procedures employed in this project have been given.

Chapter 3 contains a discussion of relevant theoretical background and methodologies for treatment of potentiometric and polarographic data collected in this research project. The methodologies for nonlinear curve–fitting models proposed in this project, and derived from appropriate equations from literature, for analysis of DC polarographic curves with reversible or non–reversible electrode reactions, have been presented.

In Chapter 4 details of the development of a computer–controlled automated instrumentation capable of DC polarographic and potentiometric data acquisition (the first aim of the project) have been given. Detailed descriptions of the hardware used, the dedicated software developed as well as the overall interfacing, performance, and validation of the instrumentation has been presented. The validation results have also been presented and discussed in relation to the applicability and limitations of the instrumental set–up.

In Chapter 5 the results and discussion related to application of the nonlinear curve–fitting models, derived and presented in Chapter 3 for analysis of DC polarographic curves from metal–ligand systems with non–reversible electrode reactions, have been presented. The validity and limitations of the proposed methodologies have also been highlighted.

In the final chapter (Chapter 6), an overall summary of important conclusions from this project has been given. Moreover, recommendations and proposed future research activities have also been outlined.

Each chapter ends with a list of references that have been cited in the main text of the given chapter.

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