

**THE THERMODYNAMICS OF COMPLEXATION OF THE LIGAND
KELEX 100 WITH VARIOUS METAL IONS**

by

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To my wonderful parents

ABSTRACT

The experimental work conducted in this thesis was aimed at determining the thermodynamic quantities associated with the formation of complexes formed between various metal ions and KELEX 100[®], a ligand which is used commercially for liquid - liquid extraction.

In order to accomplish this, the heats of protonation of the ligand KELEX 100 were determined calorimetrically at 25°C in a partially aqueous medium of 75% (v/v) 1,4-dioxane and at an ionic strength of 0.1 mol dm⁻³. Extraneous heat effects that usually accompany complex formation were accounted for by measuring each heat contribution separately.

The complexation of the lead (II), cadmium (II) and nickel (II) ions with KELEX 100 was studied in 75%(v/v) 1,4-dioxane medium. The enthalpies of complexation were measured calorimetrically and calculated using the program LETAGROP KALLE. These results were combined with the values of the Gibbs free energies available in the literature for these systems to yield the entropies of complexation. In all calorimetric determinations a constant ionic strength of 0.1 mol dm⁻³ and a temperature of 25°C was maintained.

The calculated enthalpies and entropies are discussed in terms of a number of factors that affect the thermodynamics of the systems. These factors include the structure of the ligand molecule, the nature of the donor atoms, the degree of substitution on the ligand and the properties of the metal atom such as charge and size, and the nature of the solvent.

The cumulative enthalpies and entropies of formation of the metal-ligand complexes are favourable, i.e. complexation is accompanied by a decrease in enthalpy and an increase in

entropy. However, the enthalpy changes contribute more to the stability of the complexes and hence are the driving forces for complex formation. In the case of the Cd(II) ion, the enthalpy and entropy changes are similar.

The cumulative enthalpies of formation increase (i.e., become more exothermic) in the order:



while the reverse order is found for the entropies of formation. The smaller enthalpy change for the Cd(II) complex is possibly due to the weak interaction between the 'soft' Cd(II) ion and the 'hard' KELEX 100 ligand while the decrease in entropy for the Ni(II) may be due to the loss of fewer solvent molecules from the Ni(II) hydration sphere on complexation with the ligand.

The stepwise entropy and enthalpy changes for the formation of the ML^+ complexes are dependent on the ionic radius of the metal ion. However, no linear correlations exist between the cumulative entropy or enthalpy changes of formation of the ML_2 complexes and the size of the metal ion.

The stepwise and cumulative enthalpies of formation appear to be largely independent of steric effects of the bulky alkyl substituent on the KELEX 100 ligand. The increased steric hindrance of the substituent decreases the cumulative entropy change for the formation of the Ni(II) complexes. However, in the case of the Pb(II) complexes, steric effects do not appear to affect the cumulative entropies of complex formation.

PREFACE

The experimental work described in this thesis was carried out in the Department of Chemistry and Applied Chemistry, University of Natal, Durban, under the supervision of Dr B.S. Martincigh.

These studies represent original work by the author and have not been submitted in any form to another university. When use has been made of the work performed by others, it has been duly acknowledged in the text.

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CHAPTER ONE

INTRODUCTION

The application of the chemistry of solvent extraction to industrial processes can be achieved only if the system is well characterised with respect to the distribution of species in solution, the experimental conditions of extraction and the thermodynamic quantities associated with the complexation of the extractant to the metal ion. The latter factors allow a clearer understanding of the driving processes of the complexation reaction. The aim of this thesis is to determine the enthalpies and deduce the entropies of the complexation reaction between a solvent extractant and various metal ions. This chapter serves as an introduction to the metal - ion ligand systems studied, as well as a brief introduction to the ligand and its uses. The determination of enthalpies of reaction by thermometric titration is described as well as the experimental conditions used in this work. The relative contribution of the enthalpy and entropy to the stability of the complexes is discussed.

1.1 The ligand KELEX 100 and its use in solvent extraction

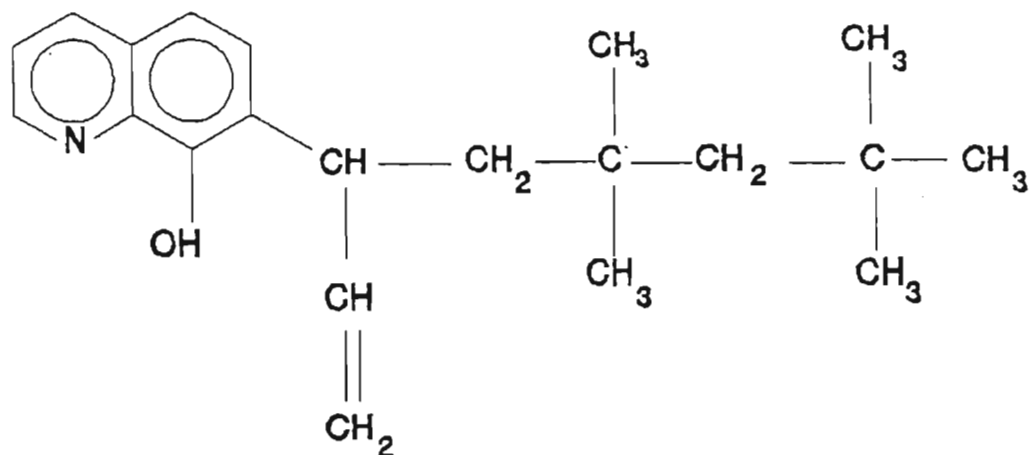
Solvent extraction is a method of separating the components of a solution by distributing them between two immiscible liquid phases. A desired metal ion is preferentially extracted from an aqueous mixture by chelation to an extractant into an organic phase. The metal ion is recovered by back extraction (or stripping) with an appropriate reagent from the organic phase into another aqueous phase called the strip liquor. Provided that optimum operating conditions are identified and the correct extractant chosen, solvent extraction can be a

highly selective and efficient method of separation and purification and finds particularly extensive applications in the chemical, mining and effluent-treatment industries. It is important to understand the fundamental driving processes that govern the selective extraction of metals, especially in the case of high cost and rarer metals such as the platinum group metals (PGM) and the rare earth metals.

The solvent extractant investigated in this work is the commercially available KELEX 100[®]. The KELEX[®] range of solvent extractants are produced by several companies, including Schering, Sherex Chemical Company and the Ashland Chemical Company. It encompasses a group of 7-alkyl-8-hydroxyquinoline derivatives under the trademark KELEX[®] [1]. KELEX 100[®] has the systematic name of 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline and is produced by the reaction of an alkenyl chloride with 8-hydroxyquinoline [2]. The metal-chelate complexes are highly soluble in organic solvents but practically insoluble in water.

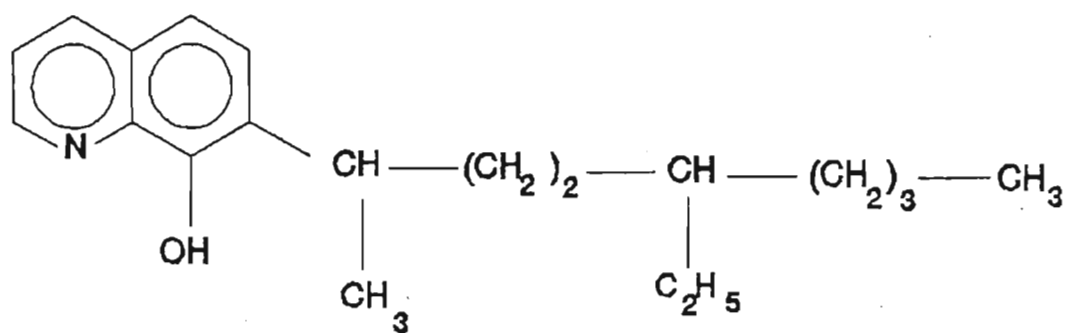
KELEX 100[®] is a chelating metal extractant which was originally designed in 1968 as a specific extractant for copper from acidic leach liquors [3]. However, this was not commercially successful due mainly to acid pickup during stripping in the solvent extraction process [4]. Despite this, it has been widely used in fundamental solvent extraction investigations of extractions of metal ions [5-13]. It is the preferred extractant for Ga(III) [14], Ge(IV) [15] and Cu(I) [16].

In 1976, the manufacturing process for KELEX 100[®] was changed such that the active component became 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline. Prior to 1976, the active component was 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-hydroxyquinoline. These structures are shown in Figure 1.1. This pre-1976 product had similar but not identical properties to



pre-1976 KELEX 100

7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-hydroxyquinoline



post-1976 KELEX 100

7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline

Figure 1.1 The structures of the active components in pre- and post-1976 KELEX 100.

the newer KELEX 100°. The post-1976 KELEX 100° ligand was used in this work. (The symbol ° will be omitted from now on from the name but the copyright trademark is still acknowledged.)

The KELEX 100 ligand is deprotonated by losing a proton from the hydroxy group. In the deprotonated form, KELEX 100 binds to metal ions through the nitrogen and the oxygen donor atoms. It is therefore a bidentate ligand and metal-ligand chelate complexes are formed.

Previous workers in this laboratory determined the values of the stability constants for the complexes formed by the Pb(II), Ni(II) and Cd(II) metal ions with KELEX 100 [17, 18]. It was found that the stability of the metal-ligand complexes increased as the ionic radii of the metal ions increased, i.e. in the order Ni(II) < Cd(II) < Pb(II). This was rationalised in terms of the hard-soft-acid-base (HSAB) theory which was forwarded to correlate a large amount of experimental facts [19]. According to this theory, metal ions are classified as 'hard' or 'soft' depending on whether they prefer bonding to oxygen, nitrogen, sulphur or phosphorus. Generally, 'hard' metal ions form complexes which are governed mainly by electrostatic interactions whereas 'soft' metal ions such as Pb(II) and Cd(II) form complexes that are more covalent in character. The Ni(II) ion is generally regarded as a 'borderline' metal ion. This qualitative classification of metal ions may give some idea of the bonding characteristics of the complexes but gives no information on the thermodynamics of complex formation. The Gibbs free energy of formation, ΔG° , is readily available from the value of the stability constant (K) by:

$$\Delta G^\circ = -RT \ln K \quad (1.1)$$

The Gibbs free energies of formation only indicate the spontaneity of the process, i.e. a negative value for ΔG° indicates a spontaneous reaction. The enthalpy (ΔH°) and entropy (ΔS°) changes of a reaction are the two contributions to the Gibbs free energy given by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1.2)$$

According to this equation, just as for most equilibrium processes, complex formation is promoted by a negative enthalpy change (i.e. an exothermic reaction) and a positive entropy change (i.e. an increase in entropy).

The purpose of this work is to calorimetrically determine the enthalpies of complex formation between KELEX 100 and the Pb(II), Cd(II) and Ni(II) metal ions. The Gibbs free energy of formation of these complexes has already been measured previously and hence by equation (1.2), the entropy of complexation can then be deduced. A knowledge of the enthalpy and entropy contributions to the Gibbs free energy will help elucidate the driving processes behind complex formation.

1.2 Thermometric titrations

The determination of enthalpy changes is most conveniently carried out by a thermometric titration. A thermometric titration is defined as "a titration in an adiabatic system yielding a plot of temperature versus volume of titrant" [20]. The first paper describing thermometric titrations was published by Bell and Cowell in 1913. They added titrant incrementally from a burette and measured the resulting temperature with a Beckman thermometer [21]. There are several terms to designate the same technique viz. thermometric titrations [22], enthalpy

titrations [23], calorimetric titrations [24], thermochemical titrations [25], thermal titrations [26], thermoanalytical titrimetry [27] and thermovolumetry [28]. The first term has been adopted here since it is referred to more often in the literature.

Thermometric titrations are universally applicable because every reaction produces some heat effect. Hansen *et al.* [29] have reviewed this technique as an analytical procedure for the rapid and accurate standardisation of solutions. Under certain conditions, a single thermometric titration can be used to yield values for ΔH° , ΔS° and ΔG° [30]. By far the greatest application of titration calorimetry has been in measurements of enthalpy changes of complex formation. Barthel [31] lists various metal ion-ligand systems for which enthalpy changes have been determined by thermometric titration. The heats of successive steps in the formation of complexes have also been determined [24]. The technique can also be used in cases where Gibbs free energy titrations fail, e.g. the potentiometric titration of the neutralization of some weak acids [32]. The titration calorimetric method of determining enthalpy changes is preferred over indirect methods, such as the potentiometric determination of the variation of stability constants with temperature, since it allows direct measurement of the quantity desired.

1.3 Complex equilibria in solution

Before describing the determination of the enthalpies of complex formation in more detail we shall describe the various types of complexes which can be formed, and define some of the quantities frequently used in the discussion of complex equilibria.

In a solution containing a metal ion, M , and a ligand, L , a multitude of species may be present. The simplest complexes are the those in which the metal ion complexes with the solvent, e.g. WO_4^{2-} , or with ligands to form mononuclear complexes, ML_r . Polynuclear complexes contain two or more metal ions, i.e. M_qL_r , where $q > 1$. Polynuclear species may be homo- or hetero-nuclear depending on whether the metal ions are the same or different, e.g. $Al_2(OH)_2^{4+}$ and $UCrO_2^{4+}$ respectively. Mixed complexes also form in aqueous solution, i.e. $M_qL_rX_s$, where X is either a second ligand, the hydroxyl ion or the hydrogen ion.

Metal complexes are formed when one or more solvent molecules are replaced by a ligand molecule. The concentrations of the solvent and bulk electrolyte are generally far greater than those of the metal ion and ligand species in solution and are therefore considered to be constant. It is assumed that no interactions occur between the reacting species (in this case M and L) and the bulk electrolyte. For simplicity, a metal ion is denoted by M^{n+} (where n is the charge) although it is surrounded by a layer of solvent molecules.

In solution, a metal ion or a Lewis acid (electron pair acceptor) can react with a Lewis base (electron pair donor) to form complexes represented by the overall reaction:



The complexes that are formed can be positively charged cations, negatively charged anions or neutral complexes. In the following derivations, the charges are omitted for simplicity.

The activities of the species present at equilibrium are related to the thermodynamic equilibrium constant, ${}_a\beta_{1r}$, at a particular temperature:

$${}_a\beta_{1r} = \frac{a_{ML_r}}{a_M a_L^r} \quad (1.4)$$

The activity, a , of a species X is related to its concentration [X] by its activity coefficient γ_X :

$$a_X = \gamma_X [X] \quad (1.5)$$

Thus equation (1.4) can be written as:

$$\begin{aligned} {}_a\beta_{1r} &= \frac{\gamma_{ML_r} [ML_r]}{\gamma_M [M] \gamma_L^r [L]^r} \\ &= \frac{\gamma_{ML_r}}{\gamma_M \gamma_L^r} \cdot \frac{[ML_r]}{[M][L]^r} \\ &= \frac{\gamma_{ML_r}}{\gamma_M \gamma_L^r} \cdot \beta_{1r} \end{aligned} \quad (1.6)$$

Since the complexation reaction (1.3) is carried out in a medium of constant ionic strength, μ , the activity coefficients of each of the species in solution will be approximately constant. Thus the activity coefficient quotient is also a constant and ${}_a\beta_{1r}$ will be proportional to β_{1r} .

The concentration quotient, β_{1r} :

$$\beta_{1r} = \frac{[ML_r]}{[M][L]^r} \quad (1.7)$$

will thus be a constant for a given reaction at a constant temperature and ionic strength and is known as the cumulative stability constant.

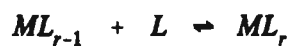
Now, equation (1.3) represents the overall reaction which can also be expressed as a series of r steps:



•

•

•



and the equilibrium constants or stepwise stability constants, K , for each step may be represented as:

$$K_{11} = \frac{[ML]}{[M][L]},$$

$$K_{12} = \frac{[ML_2]}{[ML][L]},$$

•

•

•

$$K_{1r} = \frac{[ML_r]}{[ML_{r-1}][L]}.$$

The cumulative stability constants are calculated from the product of the stepwise stability constants as follows:

$$\beta_{11} = K_{11}$$

$$\beta_{12} = K_{11} \cdot K_{12}$$

•

•

•

$$\beta_{1r} = K_{11} \cdot K_{12} \cdot \dots \cdot K_{1r}$$

$$= \prod_{i=1}^r K_{1i}$$

Thermodynamic equilibrium constants referring to the standard activity scale can be obtained, amongst other methods, by determining equilibrium constants at different ionic strengths and then extrapolating to infinite dilution. The basis of this method is the Lewis-Randall principle according to which, in dilute solutions, the activity coefficient of a given solute is the same in all solutions of the same ionic strength [34]. Potentiometry provides a convenient method of measuring stability constants in systems at a particular ionic strength and temperature. The

basis of the constant ionic medium is Brønsted's principle which states that the activity coefficients of all solutes present as small fractions of the total electrolyte concentration are constant at total electrolyte concentration [35]. Values of the stability constants can be used to deduce the Gibbs free energy of formation by the following equation:

$$\Delta G_i = -RT \ln K_i \quad (1.8)$$

where R is the universal gas constant ($8.313 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (in degrees Kelvin) and K is the equilibrium concentration constant. Measurement of the enthalpies of complex formation, ΔH , must be carried out under identical conditions as for the Gibbs free energy data so that the two may be combined to yield the values of entropies of reaction.

1.4 Titration calorimetric method of measuring enthalpy changes

As mentioned previously titration calorimetry is the preferred manner for the determination of the enthalpy changes accompanying complex formation, i.e. for studying reactions such as those to be investigated here. Titration calorimetry involves the titration of one reactant into another and the temperature or heat evolved is measured as a function of the amount of titrant added. This heat may be as a result of the chemical reaction or the physical interaction between the two solutions. The resulting data is generally presented in the form of a thermogram, that is, a plot of temperature (or heat) versus amount of titrant added, which can be analyzed to determine the heat of reaction. This type of titration can also be carried out by performing separate experiments where one reactant (titrate) is added to a series of increasingly more concentrated solutions containing the titrant. The type of data acquired is the same as that obtained by direct thermometric titration.

There are basically two types of calorimeters: batch and flow. In the batch calorimeter, one reactant solution is added to another and the temperature change or heat effect is recorded. In a flow calorimeter, both solutions are simultaneously mixed in a reaction cell and the rate of heat generated is measured. A major advantage of the flow calorimeter over other types is that the mixing fluids can be completely contained in a small mixing chamber which has a reasonably fast temperature response time. Contact with the atmosphere is avoided and

there is also the absence of a vapour phase; hence no correction need be made for enthalpy effects of condensation and evaporation, especially for volatile liquids such as 1,4-dioxane.

In this work a flow calorimeter was used.

There are two methods by which flow calorimeters can be used as titration calorimeters:

- (i) Both reactant solutions are pumped through the calorimeter until the heat generated remains constant. The pump flow rates are changed until another point is obtained. The process is repeated several times until a series of points at different flow rate ratios are obtained. The points can be arbitrarily close together.
- (ii) A series of increasingly more concentrated solutions of one reactant is made up and allowed to react in separate experiments with the other reactants.

The disadvantage of the first method is that a greater turbulent heat is generated at higher flow rates for which individual corrections would have to be made. It is usually necessary to work with dilute solutions in microcalorimetry and this implies that high flow rates would be required to allow a sufficient amount of material to react. However, the design of flow calorimeter reaction cells generally limits the maximum flow rate to fairly low values ($< 40 \text{ ml hr}^{-1}$). Low flow rates are also not desirable since the peristaltic pumps are erratic at low flow rates. Also, the method requires that the pumps be accurately calibrated to produce reproducible flow rates. The disadvantage of the second method is that it is laborious and time-consuming but is largely independent of the efficiency of the pumps since the actual flow rates are measured after each experiment. In this work, the second method was used.

The data obtained is then corrected to account for extraneous heat effects. This is described in Section 5.1. This 'corrected' data is then processed by a computer program (in this case LETAGROP KALLE (see Section 5.2.2)) which corrects for the contributions of reactions other than the reaction of interest (provided that their ΔH° values are known) and then calculates the ΔH° of the reaction required.

There are two major requirements for titration calorimetry to be successful:

- (i) the reaction enthalpy must be reasonably large, i.e. $|\Delta H| > 30 \text{ kJ mol}^{-1}$, and
- (ii) the reaction must be relatively fast compared to the time scale of the analysis and the rate of heat transfer of the calorimetry system.

In many cases and especially in this work, the nature of the solvent is not critically important and a mixed solvent system is often beneficial because of the lower heat capacity than water; hence the temperature changes are sometimes up to four times larger [33].

1.4.1 Calculation of the enthalpy change of complex formation

Generally, in a titration calorimetric experiment, the calorimetric data is collected and a thermogram is constructed, i.e. a plot of titrant added versus temperature. The data is analysed by graphical methods of extrapolation or interpolation [33]. The limitation of these methods is that the reactions must be fast and complete. Also, they are useful only in simple systems where one reaction predominates and one can only determine the overall heat of a complex reaction. Hence, this method is not applicable in systems where several complexes may form.

In the latter case, the resulting thermogram obtained has been analysed mathematically by Christensen *et al.* [30] and can be described by a set of equations. The data collected for a system containing several complexes can be used together with the equations to calculate thermodynamic quantities. This forms the basis of the "entropy titration" described by Christensen *et al.* [30] where the values of K , ΔG , ΔH and ΔS can be obtained from a single calorimetric experiment. The basis of this method will now be described.

For a simple reaction,



the total heat generated, Q , is given by:

$$Q = n\Delta H \quad (1.9)$$

where n is the number of moles of product formed and ΔH is the reaction enthalpy at a given temperature and ionic strength.

This equation can also be written as:

$$Q = V[AB]\Delta H \quad (1.10)$$

where V and $[AB]$ are the final volume of the reaction solution and the concentration of AB respectively.

As stated previously at a fixed ionic strength, the equilibrium constant of the reaction is given by:

$$K = \frac{[AB]}{[A][B]} \quad (1.11)$$

Now, one can write mass balance equations for the reactants A and B:

$$[A]_T = [A] + [AB] \quad (1.12)$$

and

$$[B]_T = [B] + [AB] \quad (1.13)$$

where $[A]_T$ and $[B]_T$ are the total concentrations of A and B respectively. Combining equations (1.11), (1.12) and (1.13) yields:

$$K = \frac{[AB]}{([A]_T - [AB])([B]_T - [AB])} \quad (1.14)$$

Equation (1.14) can also be written as a quadratic in $[AB]$,

$$K[AB]^2 - (K[B]_T + K[A]_T + 1)[AB] + K[A]_T[B]_T = 0. \quad (1.15)$$

Inversion of equation (1.14) and some rearrangement yields,

$$\frac{1}{K} = \frac{[A]_T[B]_T}{[AB]} - ([A]_T + [B]_T) + [AB]^2 \quad (1.16)$$

which, after substitution of equation (1.10) and multiplication by ΔH , gives:

$$\frac{\Delta H}{K} = \frac{[A]_T[B]_T V}{Q} (\Delta H)^2 - ([A]_T[B]_T) \Delta H + \frac{Q}{V}. \quad (1.17)$$

Equation (1.17) reduces to the form,

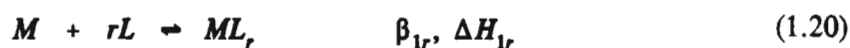
$$\frac{\Delta H}{K} = X(\Delta H)^2 + Y(\Delta H) + Z. \quad (1.18)$$

Since ΔH and K do not change for a given reaction at constant temperature and ionic strength, $\Delta H/K$ is the same for every point on the thermogram and can be eliminated by combining any two points to yield:

$$(X_2 - X_1)(\Delta H)^2 - (Y_2 - Y_1)\Delta H + (Z_2 - Z_1) = 0 \quad (1.19)$$

where ΔH can be readily obtained and hence K can be calculated.

Extending this discussion to a system where a metal ion is titrated with a ligand, the following overall reaction describes a system of r consecutive equilibrium steps:



where β_{1r} is the cumulative stability constant for the r th species defined as in Equation (1.7) and ΔH_{1r} is the associated cumulative enthalpy change.

Also,

$$[M]_T = [M] + [ML] + [ML_2] + \dots + [ML_r] \quad (1.21)$$

$$[L]_T = [L] + [ML] + 2[ML_2] + \dots + r[ML_r] \quad (1.22)$$

where $[M]_T$ and $[L]_T$ are the total metal ion and ligand concentrations respectively.

Combining these equations, one can solve for $[L]$. However, the analytical solutions, although exact, yield unwieldy expressions for large values of r and are laborious to calculate. $[L]$ can also be solved for by Newton's method of approximation and the concentration of the other species present can then be calculated from the equations. The original approach to the solution was to use a system of simultaneous equations but after some refinements and criticisms of the methods, a method of least squares was adopted [36]. The principle of this type of analysis is to minimise the sum of the squares of the differences between the experimental and theoretical curves which result from the selection of ΔH and K . Given values of K and ΔH , one may compute Q_t , a theoretical value of the heat generated at any volume of titrant added and determine a function $U(K, \Delta H)$ such that,

$$U(K, \Delta H) = \sum w_i (Q_{\text{exp}} - Q_t)^2. \quad (1.23)$$

where w_i is the number of different reactions.

It is then possible to vary K and ΔH in some systematic fashion to minimise $U(K, \Delta H)$. Due to the non-linearity of the relationship among Q , ΔH and K , it is not possible to solve an explicit equation for the desired values of the parameters as can be done in a linear least-squares problem. Thus, an iterative procedure to find U_{min} must be used.

There are two possible procedures:

- (i) Plot the entire surface $U(K, \Delta H)$ by using assumed values of K and ΔH to compute Q_t and eventually U from the equation. Once a set of contours are drawn, the function can be inspected for a minimum. This is obviously an extremely laborious procedure which is of limited practical use.

- (ii) Use a procedure called the "pit-mapping" technique which is incorporated in the LETAGROP KALLE computer programs used in this work [37].

Arnek [38] has described the latter procedure as applied to calorimetry in detail. Due to the iterative nature of the problem, one is forced to assume a functional relationship between U and the unknown parameters. In general, a quadratic relationship is assumed. Obviously, a parabolic function is the lowest degree polynomial which is capable of having a relative minimum. The error surface (U) is well represented by such a function only in the vicinity of a minimum; it is therefore necessary to assume an initial value of all the sought after parameters. Obviously, the better the guess, the faster will be the convergence.

In this work, the minimisation was simplified as the K values were measured by previous workers and hence only initial guesses for ΔH were required. The values of ΔH corresponding to the given value of K can then be evaluated using the minimisation expression, i.e.

$$\frac{\delta U(K_p \Delta H_i)}{\delta \Delta H_k} = \sum_{p=1}^m Q_{\text{exp},p} \Delta n_{k,p} - \sum_{p=1}^m \Delta n_{k,p} \sum_{i=1}^n (\Delta n_{i,p} \Delta H_i) = 0 \quad (1.24)$$

where m is the number of data points, i is the type of product formed and $\Delta n_{i,p}$ is the number of moles of product i formed.

1.5 Thermodynamics of complex formation

The relative stabilities of complexes are usually interpreted in terms of only the ligational free energy changes, i.e. those which accompany complex formation. Complex formation is favoured by a negative enthalpy change (i.e. an exothermic reaction) and a positive entropy change. The factors which affect the solution stability of chelate complexes may be divided into enthalpy and entropy effects. These factors are listed in Table 1.1. To obtain these contributions to the Gibbs free energy change, these quantities must be measured. In this work, since the Gibbs free energies were known, only the enthalpies were measured and the entropies were obtained from equation (1.2).

There is much debate in the literature as to whether the enthalpy or entropy changes is the driving force behind complex formation. This is further fuelled by the experimental observation that the complexes formed are more stable than the corresponding complexes formed with monodentate ligands has been dubbed the 'chelate effect'. Martell *et al.* [40] demonstrated that, when two or more atoms are tied together to form an additional chelate ring without materially affecting the donor groups, the increased stability of the chelate, as reflected in the formation constant, is due almost entirely to an increase in entropy. Further, they pointed out that the greater part of the entropy increase is directly related to the formation of chelate rings. Calvin *et al.*[41] found out that the replacement of ammine ligands by the bidentate ethylenediamine ligand with Ni(II) results in a free energy change to which the enthalpy and entropy contributions are approximately equal. Williams [42], on the other hand, asserted that the decrease in enthalpy associated with metal complex formation can account for the increased stability of chelate complexes. Thus there are several differing arguments for the enhanced stability of chelates and this has been further complicated by the

Table 1.1

Enthalpy and entropy factors influencing solution stabilities of chelate complexes. (This table is taken from Table 1 in Reference 39.)

Enthalpy effects	Entropy effects
Variation of bond length with electronegativities of metal ions and ligand donor atom	Number of chelate rings
Ligand field effects	Size of chelate ring
Steric and electrostatic repulsion between ligand donor groups in the complex	Changes of solvation upon complex formation
Enthalpy effects related to the conformation of the uncoordinated ligand	Arrangement of chelate rings
Other coulombic forces involved in chelate ring formation	Entropy variations in uncoordinated ligands
Enthalpy of solution of ligands	Effects resulting from differences in configurational entropies of the ligand in complex compounds
Change of bond strength when ligand is changed (same donor and acceptor atom)	Entropy of solution of ligands
	Entropy of solution of uncoordinated metal ions

influence of other factors such as the solvent medium and the nature of the metal ions and ligands.

The effect of enthalpy and entropy contributions to the Gibbs free energy must be considered separately to understand a system. There is a dearth of precise thermodynamic data on chelate formation. Prior to 1959, the majority of enthalpies were measured indirectly by the temperature dependence of stability constants which gave, at best, values with precisions of between 2-8 kJ mol⁻¹ [43]. Despite the lack of reliable values, certain trends are apparent. For many reactions, enthalpy and entropy contributions favour complex formation but their relative importance changes markedly with minor variations from ML to ML' or M'L. The equilibrium constant, K, and hence the Gibbs energy, consists of a unitary part which is characteristic of the reactants and a cratic part which depends solely on the numbers of the interacting species. For some reactions, either the enthalpy or entropy change may oppose complex formation, although negative entropy changes will largely be due to the cratic term [44].

1.5.1 Entropy of complex formation

The entropy change on complex formation is expected to be negative due to the conversion of translational to vibrational and rotational entropy [45]. Polyatomic atoms will undergo an additional loss of rotational entropy. Association of a metal ion with a unidentate charged ligand in aqueous solution is accompanied by a decrease in the number of ions, partial neutralization of electrical charge, attenuation of the remaining charge and by displacement of water molecules from the hydration spheres of the reactants. It was shown by several workers that ligational entropy changes are usually positive but this is not always the case

[46-49].

The role of the solvent medium is also important in trying to rationalize ligational entropy changes. The degree of solvation of the metal ion and the ligands will contribute to the magnitude of the entropy change. Displacement of solvent molecules from a poorly solvated ion will result in smaller entropy gains than displacement from a strongly solvated ion.

For aqueous systems, chelation by a multidentate ligand is accompanied by a loss in configurational entropy, but more water will be displaced from the hydration sphere of the reactants. The entropy change associated with chelation is greater than that associated with the formation of a similar non-chelate complex and greater for a charged than a neutral chelating ligand [45].

The ligational entropy change, ΔS° , will depend on standard entropies in solution of the complex, $\Delta S^\circ(ML_r)$ and of the metal ions, $\Delta S^\circ(M)$, and ligands $\Delta S^\circ(L)$. For mononuclear complex reactions, the standard entropy change is given by:

$$\Delta S_r^\circ = S^\circ(ML_r) - S^\circ(M) - rS^\circ(L) \quad (1.25)$$

$S^\circ(M)$ and $S^\circ(L)$ values for monatomic cations and anions are well established [50]. Values are related empirically by the Powell [51] or Cobble [52] equations of the form:

$$S^\circ = A - B\frac{z}{r^2} \quad (1.26)$$

which do not contain explicit translational terms. Parameters A and B depend on the particular functions of ionic radius r chosen and z is the ionic charge. Other empirical

correlations have been developed for standard entropies of polyatomic ligands, using parameters that incorporate structural factors, molar volumes, atomic masses, ionic radius etc. (for examples, see references 53-55). Much more thermochemical data is required to fully elucidate structure/entropy relationships.

1.5.2 Enthalpy of complex formation

Unlike ligational entropy and Gibbs free energy changes, the enthalpy is a unitary quantity. The larger, exothermic heat changes that accompany the formation of essentially covalent bonds, especially for transition metal cations, may often have appreciable double bond character.

Ligational enthalpies in aqueous solution are the small heat changes which accompany the replacement of water by other ligands. No attempt has been made in the literature to predict values of ΔH by means of standard enthalpies of reactants. Williams [49] suggested that ligational enthalpy changes should be represented by an equation of the form:

$$\Delta H = A \frac{z}{r_M} + BI_2 - \frac{C}{r_M^3}$$

where I_2 is the second overall ionisation potential, r is the radius of the ion, z is the charge on the ion and A , B and C are parameters used to fit experimental data to the equation.

The enthalpy changes accompanying complex formation are also dependent on the degree of solvation of the reactants in the solvent system. This can be illustrated by the thermodynamic quantities associated with the replacement of solvating water molecules by ammonia in the

Cu(II) hydration sphere: the enthalpy of hydration of Cu(II) is $-2100 \text{ kJ mol}^{-1}$ whereas the enthalpy change for the reaction itself is only -92 kJ mol^{-1} , i.e. an order of magnitude less than the solvation energy [49].

Uusitalo [56] was able to represent values of ΔH_1 for the reactions of a number of 7-phenylazo- and 7-(4-nitrophenylazo)-substituted 8-hydroxyquinoline-5-sulphonic acids in this way and found a correlation with the electronegativity, χ^M , of the metal ion. However, Charles [57] could not so represent 13 values of ΔH_1 for M(II)-ethylenediaminetetraacetato complexes and found no single correlation with metal ion electronegativity but instead a correlation with $z\chi_M r_M$, where r_M is the radius of the metal ion and z is the charge.

The heats of formation in the gas phase ΔH_g of complex ions of the transition series may be rationalized by the ligand field theory [58]. In the presence of an octahedral field due to six ligands, the five-fold degenerate d orbitals of a transitional metal ion split into a d_e triplet of lower energy and a d_v doublet of higher energy. The energy separation Δ (or $10Dq$) between the two levels is approximately 120 kJ mol^{-1} for bivalent aquo ions. Ions with the configurations d^0 , d^5 and d^{10} will be essentially spherical, of decreasing size due to increasing nuclear charge, and ΔH_g will be expected to vary smoothly with atomic number. In high-spin complexes, the d^1 , d^2 , d^3 , d^6 , d^7 and d^8 electrons will occupy d_e levels and confer a stabilization of approximately 5 per cent in excess of the regular change from d^0 through d^5 to d^{10} . The d^4 , d^5 , d^9 and d^{10} electrons are forced to occupy the d_v levels and the extra stabilization is cancelled out. The orbital stabilizations for the d^0 , d^1 , d^2 , d^3 , d^4 and d^5 ions are 0, 0.4Δ , 0.8Δ , 1.2Δ , 0.6Δ and 0, and the sequence is repeated in the second half of the transition series.

Metal ions with d^4 or d^9 configurations, e.g. Cr(II) and Cu(II), usually adopt a tetragonally distorted octahedral configuration which confers extra stability. This is due to the Jahn-Teller effect.

From the foregoing discussion, it is expected that the ligational enthalpy change for the complexation reaction in solution will vary smoothly with atomic number for the d^0 , d^5 and d^{10} ions, but the enthalpies for the intermediate ions will be higher. On this basis, the predicted sequence for the negative enthalpies of formation of bivalent transitional metal ions would be:

$$d^0 < d^1 < d^2 < d^3 < d^4 > d^5 < d^6 < d^7 < d^8 < d^9 > d^{10}$$

Deviations from the above would occur if the ligands form strong π bonds, or if the ground state of the metal ion is changed on complex formation.

1.5.3 Gibbs free energy of complex formation

The free energy changes that accompany complex formation are a measure of the stability of the complex, i.e. a larger negative free energy change indicates higher complex stability. In general, the stability of metal-ligand complexes depend on the properties of the metal and the ligand. Metal ions that form complexes are usually of three kinds, viz. metals which form ions of noble gas structure, or ions with an outer shell of 18 electrons, or transition metal ions. The properties of the ligand vary much more widely due to the potentially large number of ligands capable of complexing with metal ions. Complex stability is dependent on several properties of the ligand [59,60]:

- (i) Nature of the ligand atom - atoms which are bound directly to the metal ions in complexes are those of the more electronegative elements on the right side of the periodic table, e.g. C, N, S. Any of the ligand donor atoms may coordinate with a metal ion.
- (ii) Basicity - when a ligand shows basic properties with respect to water as a solvent, a correlation is often noted between the base strength (i.e. proton affinity) and the stability of its metal complexes (i.e. cation affinity).
- (iii) Chelation - the formation of a chelate ring increases the stability over comparable complexes where chelation is not possible. The chelate effect is the result of both enthalpic and entropic contributions. The enthalpic effect is because the electrostatic repulsion, resulting from placing two negatively charged ligand atoms in close proximity, has already been largely overcome if the ligand atoms are close together in the same molecule. Also, the enthalpy changes appear to be related to the ligand field stabilization. Thermodynamic data show that enthalpies are almost negligible for Zn and Cd in which there is no ligand stabilization, but are more important for nickel and copper complexes [61]. The entropy effect arises because, when one end of the ligand is already attached to the metal centre, there is no further sacrifice of translational entropy accompanying the attachment of the subsequent ligating atoms because the number of particles in the system does not change. The sacrifice of configurational entropy is small for the formation of rings with six or less members but increases rapidly with increasing ring size with a concomitant disappearance of the chelate effect [62]. It is also believed that the chelate effect can be regarded thermodynamically as an entropy effect where a solvated metal ion in solution

reacting with a chelating ligand displaces solvent molecules in the coordination sphere of the metal ion and thus increases the number of molecules present, e.g. the displacement of H_2O molecules from $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ by 3 molecules of ethylenediamine results in a net increase of 3 molecules. However, it is not exclusively an entropy effect since this implies that $\log K$ would be almost independent of the metal ion, which has been shown to be incorrect [63].

- (iv) Steric effects - these are associated with the presence of a bulky group either attached to or near enough to a donor atom to cause mutual repulsion between the ligands and a weakening of the metal-ligand bonds, e.g. metal complexes of 2-methyl-8-hydroxyquinoline are less stable than those of 8-hydroxyquinoline or 4-methyl-8-hydroxyquinoline.

These relative contributions of enthalpy and entropy to the free energy depend largely on the structure of the chelating agent, the nature of the metal ion and, to some extent, the solvent medium.

1.5.3.1 Influences of the structure of the chelating agent

Several properties of chelates are determined by the nature of the chelating agent which combines with the metal ion. Thus the chemical structure and bonding within the chelating agent plays an extremely important role in governing the stability of the resultant complex [64].

- (a) Size of the chelate ring - Four-membered chelate rings in a complex are seldom encountered. Five- and six- membered rings are usual. In general, 5-membered rings are more stable than 6-membered rings in solution. Further, it is also observed that 5-membered rings are more stable when completely saturated and 6-membered rings when there are double bonds, but there are notable exceptions. Depending on the chelating ligand, the size of the ring may decrease stability when there is strain in a small ring.
- (b) Number of rings - depending on the geometric compatibility of the metal ion and ligand, the stability of complexes of multidentate ligands increases with the number of chelate rings formed, e.g. the stability of a series of bivalent metal ion complexes of a series of closely related polyamines increases with the number of nitrogen donor atoms [65].
- (c) Resonance effect - if there is resonance of double bonds in a ligand molecule, the bond order of a particular bond decreases and this is reflected in a loss of stability e.g. the Cu(I)-acetylacetonate complex is more stable than the Cu(I)-salicylaldehyde complex, where the phenolate ion of the salicylaldehyde complex can be written in two resonance forms with double bonds in alternate positions in the benzene ring.
- (d) Nature of the ligand donor atom - Although some M-L bonds can be described adequately by a coulombic model, it is usually necessary to consider homopolar contributions as well. In most transition metal complexes a donor atom donates a lone pair of electrons to an acceptor orbital of the metal ion. The donation may involve some π character, particularly if the transition metal ion has a few d .

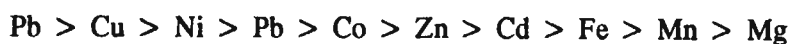
electrons under its valency shell. The majority of metal ions form their most stable complexes with the donor atoms C, N, O and F. In general, donor atoms which give large ligand field splittings form their strongest complexes with metal ions which are particularly sensitive to ligand field stabilization, whereas donor atoms which produce small ligand fields tend to form relatively more stable complexes with cations that are insensitive to ligand field stabilization. The effect of the donor atom is difficult to assess since changes in the donor atom are usually accompanied by other effects such as changes in basic strength, steric factors, size of chelate ring, etc. Probably the dominant effect of the donor atom is the change in basic strength. The stabilities of complexes formed by ligands containing a particular donor atom depend on the metal ion the ligand complexes with, e.g. oxygen donor ligands are more stable than nitrogen donor ligands in complexes of Mg and Ca but the opposite is observed for Cu(I) and Ag(I).

- (e) Effect of substitution on the ligand - The substitution of a group on the chelating agent may affect the tendency for chelation in one of two ways: (i) it may influence the acidity of the donor groups, or may interfere with or enhance the resonance of the chelate rings, or (ii) the addition of groups on the ligand may, by purely steric effects, prevent the ligand ions or molecules from acquiring the orientation about the central metal ion most favourable for chelation. The conjugate bases of strong acids form weak complexes with metal ions and vice versa. A correlation is expected between the stabilities of the hydrogen ion and the metal ion complexes, since the metal ions function as Lewis acids. Several studies seem to confirm this and correlations have been made with the stability of the first protonation of a multidentate ligand. The deviation from linearity may be ascribed to considerations

of enthalpy and/or entropy. Enthalpy changes which accompany the formation of proton complexes mainly reflect differences in σ -electron density on the donor atoms, whereas those accompanying the formation of metal complexes will be affected by π bonding between metal ion and ligand, and will also be more sensitive to steric hindrance. The entropy changes which accompany the association of protons with anions are roughly equal, according to the Pitzer rule, but those accompanying their association with amines and related ligands are more variable [66]. Substitution of bulky groups onto ligands will be expected to increase the structure-breaking effect of a metal complex on a solvent, and possibly to shield the coordinated metal from contact with the solvent. The major deviations from linearity between $\log K_{HL}$ and $\log K_{ML}$ increase with the size of the substituent on the ligand and have been ascribed to steric hindrance, e.g. among 2-hydroxyquinolinates [67].

1.5.3.2 Effect of the metal ion on stability

The stability of complexes containing a particular chelating agent is dependent on the nature of the metal ion. Mellor *et al.* [68] showed that the stability of bivalent metal ions loosely follow the order:



irrespective of the nature of the ligand. As an approximation, the stability decreases with the increasing basicity of the metal. This suggests that the strength of the bonding in these chelates depends on the ability of the metal to form homopolar bonds. These stabilities can be correlated with the ionisation potential or, more generally, with some property related to the atomic number of the metal. Thus, the factors which influence stability include: (i) the ionic forces which are related to both the charge and radius of the metal ion, (ii) the atomic

number of the metal, (iii) the ionisation potential and electronegativity, and (iv) the stereochemistry of both the metal ion and the ligand.

- (i) Charge and radius - the influence of the charge and radius of the metal ion can be deduced from the Born equation developed to relate the energy of solvation of metal ions to the properties of the ion [69]:

$$\Delta E = \frac{e^2}{2r} \left(1 - \frac{1}{D}\right) \quad (1.28)$$

where e is the charge on the metal ion, r is the radius of the ion, ΔE is the energy change and D is the dielectric constant of the solvent.

For ionic chelates such as those formed by the alkali and alkaline earth metals, the strength of chelation should increase with increasing ionic charge of both the metal ion and donor and increase with decreasing ionic radius of the metal ion, i.e. an increase in stability with an increase in charge-to-radius ratio.

- (ii) Atomic number - the correlation of $\log K$ for complexes with the atomic numbers of the central metal ions of the first transition series for a wide variety of ligands which coordinate through O and N atoms follows the sequence:



which is similar to that observed experimentally by Mellor *et al.* [68].

- (iii) Ionisation potential and electronegativity - for complexes of bivalent metal ions, it has been shown that there are linear correlations between the first [70] or second [71]

step-wise ionisation potential or the second overall ionisation potential [72]. It has also been demonstrated that rough linear correlations exist between stability constants and electronegativities of the metal ions although these trends are more qualitative in nature.

- (iv) Stereochemistry - the stereochemistry greatly influences enthalpy and entropy changes, especially for highly substituted ligands. An example of the effect of stereochemistry on stability constants, and hence Gibbs free energies, is provided by the complexes of polyamines [73]. Stability constant data for the displacement of a polydentate ligand by a ligand of higher denticity show that there are optimum sizes of metal ions which yield more stable complexes and these ions differ depending on the type of ligand used, i.e. the optimum size for complexation depends on the relative stereochemistry of the metal ion and the ligand.

1.5.3.3 Effect of the solvent medium on thermodynamic properties

Most complexation reactions are studied in aqueous media. Ions in solution are postulated to have water molecules clustered around them like an 'iceberg' [74]. Upon complex formation between oppositely charged reactants which effectively removes the ions from solution, the ordered structure is broken and the entropy change is thus favourable. Generally, in the absence of complicating factors such as steric effects, the entropy change should be proportional to the entropy of hydration of the ion, which it has been roughly shown to be [75]. The entropy of hydration, S° , for all monatomic ions was shown to be:

$$S^0 = \frac{3}{2}R \ln M + 37 - 270 \frac{z}{r_e^2} \quad (1.29)$$

where M is the atomic mass, z is the charge, and r_e is the effective radius of the ion.

It is predicted that the entropies of complex formation can be related to the enthalpies of hydration of ions and some data seem to confirm this [42]. When an ion dissolves in water the entropy change is a function only of its charge and radius. Therefore the entropy of solution of various coordinated ionic species will vary with the size, with the smaller being more negative. Also, the nature of the coordinating group must be considered. If the hydrogen-bonding capability of the ligand is decreased, its entropy of solution is more negative. This treatment is, however, relevant only to aqueous systems. A large number of chelating organic ligands are sparingly soluble in water and hence a mixed organic-aqueous solvent is used to enhance solubility of complexes. The use of a mixed solvent poses an important problem. If selective solvation of a metal occurs, the association constants obtained in different media will refer to different reactions. It is probable that selective solvation of metal complexes does not occur when the mole fraction of water is greater than 0.8, as the Walden product of limiting conductivity and viscosity is constant for a number of water-rich systems [76,77]. In completely non-aqueous media, metal ions will not be hydrated and possibly not even solvated. With the possible exception of metal amines, association constants of a wide variety of metal complexes containing inorganic and organic ligands increase as the dielectric constant of the medium decreases, which is the direction expected from electrostatic considerations. This has been confirmed for several systems [78].

The simplest model for a solvent is one of a continuous dielectric which effectively reduces charge-charge interactions but does not influence the energies associated with covalent

bonding. A high value of the dielectric constant, D , of a solvent indicates that the solvent molecules are polar and will interact with ions as well as dipoles present. As the dielectric constant increases and the ionic energies diminish, then the effect of covalence in bringing about association of reactants becomes dominant. In a medium of high dielectric constant, the coulombic interaction between two oppositely charged species, A^+ and B^- , is very small. Considering the solvent as a system of molecules with high dipole moments, then the solvation of A^+ and B^- is such that A^+B^- is not stable. Water has the highest dielectric constant of all ordinary liquids, so aqueous solutions represent an extreme of low electrostatic interaction. In solvents of lower dielectric constants, the electrostatic interactions will be greater than in water. In terms of complex formation the action of a solvent is not limited to its influence upon the strength of the electrostatic interaction between acceptor and donor. The solvent will interact especially strongly with metal cations which are small and have a high charge and are thus extensively solvated. The interactions between solvent dipoles and other ligands are fairly weak in both cases.

The effect of the organic component on the association constant has not been analysed. $\log K$ has been shown to be a linear function of the mole fraction of the organic solvent for several ligands [67]. The variation of $\log K$ for a reaction performed in various solvents has been attributed to changes in electrostatic interactions as the dielectric constant, D , changes [79].

Steric factors also play a part in determining the extent of solvation. Bianchini *et al.* [80] found that interaction between metal ions and the bidentate amine ligands, NN'-diethylethylenediamine (deen) and NN-diethylethylenediamine (deae), gives rise to a positive entropy change due to the liberation of solvating water molecules. The released water

molecules were transferred from the first and second hydration spheres of the metal ion. The presence of hydrophobic alkyl groups on the nitrogen atom of the amine ligand causes a larger desolvation of the aqueous metal ion and consequently the liberation of more water molecules from the hydration sphere [81]. The extent to which this occurs is dependent on the bulkiness of the alkyl substituents; the value of ΔS is larger for the reaction of ethyl than for methyl-substituted diamines. For the same ligand, symmetrical and asymmetrical, the entropy change is larger for the asymmetrical ligand. Since the liberation of water molecules is an endothermic process, the smaller exothermic values for the reactions of Cu(II) with N-alkyl-substituted diamines must be attributed not only to the formation of weaker coordinate bonds but also to greater desolvation. High values of ΔS observed in the reactions of deen and deae confirm the bidenticity of these ligands in aqueous solution. The full coordination of the diamine causes the release of a larger number of water molecules and this is reflected in the ΔS values.

Few entropy and enthalpy data have been reported as a function of varying organic content or different dielectric constant of the solvent. This would be of interest since changes in the energetics of interaction due to both solvent effects and changing electrostatic effects would be expected to appear in the magnitude of both the ΔH and ΔS values for the reaction.

Li *et al.* [82] found that ΔH_2 is the same for bis(glycinato)nickel (II) in water and in 45% dioxane, whereas ΔS_2 is about $46.024 \text{ J K}^{-1} \text{ mol}^{-1}$ less positive in the water-dioxane mixture. This has been ascribed to selective solvation. A similarly small variation in enthalpy change but significantly different entropy change has been reported for cadmium chloride complexes in water-methanol systems [83]. However, comparison of data for complexes of substituted 8-hydroxyquinolines in water and 50% dioxane suggests significant variations in the ligational

entropies than the entropy terms [84]. Izatt *et al.* [85] found that ΔH for the ionization of water in water-dioxane mixtures followed electrostatic predictions but not $\log K_w$. For ΔH_{neut} in ethanol-water mixtures, behaviour deviated from electrostatic predictions. For the interaction between thiourea and $\text{Hg}(\text{CN})_2$, which are both uncharged, in ethanol-water mixtures, it is expected that ΔG , ΔH and ΔS should be independent of the dielectric constant. ΔG was found to be almost the same but ΔH and ΔS deviated greatly from electrostatic considerations due to solvation effects. It is thus clear that, due to the lack of sufficient thermochemical data, it is difficult to correlate enthalpy and entropy effects as a function of the organic content of the solvent medium.

1.6 Bonding considerations in complex formation

It has long been known that metal ions have particular preferences for certain ligands in aqueous solution. Schwarzenbach [86] had classified metal ions into two groups in an attempt to empirically correlate a large mass of experimental facts. Arhland *et al.* [87] extended this to the special case of metal ions as Lewis acids where the metal ion was classified according to whether it formed its most stable complexes with the first ligand atom of groups V and VI, termed class (a), or with the subsequent member of each group, termed class (b). Pearson [88] used the terms 'hard' and 'soft' to classify Lewis acids and Lewis bases. 'Hard' acids are generally small ions with a large positive charge and a rigid electron shell structure and thus not easily polarizable. 'Hard' bases are similarly non-polarizable. 'Soft' acids are usually large metal ions with a low charge and a loose electron shell structure which contains readily excitable outer electrons. 'Soft' bases are ligands which are easily polarized. The advantage of this classification is that it allows the generalization that hard acids associate with hard bases whereas soft acids associate with soft bases.

Hard acids and hard bases are held together by ionic, or polar, bonds whereas soft-soft interactions are primarily covalent [89]. Hard-soft interactions are a mismatch of bonding tendencies and generally result in weak complexes. The role of the solvent is very important in classifying acids and bases. The nature and strength of an acid or base depends on its immediate environment and degree of solvation [90]. For metal ions, however, the tendency for ionic or covalent bonding which is ultimately responsible for hard or soft behaviour will remain, as it is linked to the electronic configuration of the ion [91]. The variation of bond strength with the change in dielectric constant is more marked the higher the charges and smaller the radii of the acceptor and donor atoms involved. The resultant character of the bond depends on the relative strengths of the electrostatic and covalent interactions. A change in dielectric properties is always accompanied by a change in the solvation of the species present. Solvent molecules show particular preference for certain species, solvating them to a higher extent than would be expected from the purely electrostatic interaction arising from the dipole properties of the solvent. Thus the solvent itself can be classified as hard or soft because solute-solvent interactions can be considered as acid-base interactions of varying degree, e.g. water is a hard base that will solvate other hard bases like OH^- but other diprotic, apolar solvents like DMF, DMSO and acetone will be soft solvents.

Ligand substitution reactions which take place in complex formation are considered a special case of acid-base interactions.

Metal ions are classifiable on the basis of their polarizability and other associated properties, e.g. ionization potential. There are several scales of softness suggested in an attempt to quantify this property by a single number, with varying degrees of success [92,93]. The Cd(II) ion is classified a soft acid and both Pb(II) and Ni(II) are considered to be borderline

cases, i.e. their properties are intermediate between hard and soft character [88]. High acid polarizability is linked to low ionization potential and electronegativity. Klopman [94] showed that the softness of a Lewis acid decreases with a decrease in the dielectric constant of the solvent.

The classification of bases is more difficult since the hardness of a base is dependent largely on the donor atom on the ligand. The more electronegative the donor atom, the harder is the base. The multitude of different ligand structures make it extremely difficult to assign relative hardness characters to ligands. However, high polarizability is associated with the degree of unsaturation in the molecule and the electronegativity of the donor atom. Hard acceptors generally show strong preference for oxygen donors and thus these are considered hard. Nitrogen is classified as a softer donor because it forms complexes with most soft acceptors as well as acceptors of medium hardness. A mixed oxygen-nitrogen donor like KELEX 100 should combine the affinities of both oxygen and nitrogen and thus form strong complexes with a great variety of acceptors, e.g. for the multidentate ethylenediaminetetraacetic acid donor, the entropy dominates and contributes more to the stability. Thus the classification of KELEX 100 would be considered a hard ligand.

Reactions involving bonds of different nature are likely to have different thermodynamic characteristics. Hard-hard interactions are accompanied by charge compensation and by the release of water molecules from the hydration shell bound strongly to the ligand and to the metal ion which requires much energy which is not completely regained by the formation of a predominantly electrostatic acceptor to donor bond. Also, during the course of a charge compensation reaction, there is a lowering of the electrostatic field around the ions and this will increase the mobility of the solvent molecules exposed to these fields, increasing the

entropy. Accordingly the thermodynamic driving force of complex formation is the large positive entropy change; in comparison, the stabilizing role of the enthalpy change is insignificant. Soft donors and acceptors interact weakly with polar solvents like water and are little, if at all, hydrated. Thus there is little liberation of solvent molecules and no large entropy gain. In fact, there may be an entropy loss due to the decrease in the number of particles as well as a loss in vibrational and rotational freedom of the ligand. The formation of a markedly covalent acceptor to donor bond is accompanied by a large evolution of heat and constitutes the driving force of the reaction between soft reactants. In other solvents of lower dielectric constants than water, like 1,4-dioxane-water mixtures used in this work, the electrostatic interactions may be stronger and the stability trends may be reversed.

1.7 Outline of the project

The aim of this work is to determine the enthalpy of formation of complexes between the ligand KELEX 100 and the Pb(II), Cd(II) and Ni(II) metal ions. Combining this data with the free energies of formation which were previously determined, one can deduce the entropy changes and thus determine the driving forces for the reactions.

All systems were studied in an aqueous 75% (v/v) 1,4-dioxane medium at an ionic strength of 0.1 mol dm^{-3} and a temperature of 25.00°C , with sodium perchlorate as the background electrolyte. The enthalpies were measured calorimetrically.

In this work all thermodynamic quantities are reported at the standard state of the solute, which is at a concentration of 1 mol dm^{-3} .

CHAPTER TWO

MATERIALS

The preparation and standardization of each stock solution is described in this chapter. The volumetric glassware used was A-grade. Aqueous solutions were prepared from water that had been purified by a Millipore Milli RO-6 water purification apparatus except for NaOH solutions which were made up to volume with boiled out water. The KELEX 100 stock solution was made up in purified dioxane. The working solutions used for enthalpy measurements were prepared by appropriate dilution of the stock solutions.

2.1 Preparation and standardization of background electrolyte stock solutions

The background electrolyte used for measurements in this work was sodium perchlorate. Stock solutions of sodium perchlorate (ca. 2 mol dm⁻³) were prepared from MERCK NaClO₄·H₂O (min. 99% pure). The solution was filtered before being made up to volume due to some insoluble impurities which remained. The stock solution was standardized by passing a 5.00 cm³ aliquot through a column (i.d. 2 cm) packed to a height of 30 cm with an acidic ion exchange resin (Amberlite IR-120 (H) from BDH, particle size 0.30 - 1.18 mm (14 - 52 mesh), analytical grade). A glass wool pad was placed on top of the resin bed before use. The resin was washed with water until the eluate was neutral to a MERCK pH stick (ca. 300 cm³ water). The hydrogen ions liberated were titrated against a freshly prepared and standardized ca. 0.5 mol dm⁻³ NaOH solution by using methyl orange as indicator. The

concentration of NaClO_4 calculated from standardization was approximately 99% of the concentration calculated from the mass of solid weighed out. This discrepancy is possibly due to the undissolved residue removed by filtration.

Prior to use, the Amberlite IR-120(H) resin was converted completely to the purely hydrogen form by passing one bed volume of 2 mol dm^{-3} HCl through the column, followed by washing with water until the final 100 cm^3 of eluate required less than 1 cm^3 of 0.02 mol dm^{-3} NaOH to neutralize its acidity when methyl orange was used as indicator [95].

2.2 Preparation and standardization of stock solutions of strong acid and strong base

2.2.1 Preparation and standardization of stock solutions of perchloric acid HClO_4

Stock solutions of perchloric acid (ca. 2 mol dm^{-3}) were prepared from KLEBER HClO_4 (min 70% pure, sp. gr 1.67) and standardized by titration against freshly recrystallised borax [96].

2.2.2 Preparation and standardization of stock solutions of sodium hydroxide

Stock solutions of sodium hydroxide (ca. 1 mol dm^{-3}) were prepared from MERCK 1 mol l^{-1} TITRISOL ampoules and made up with freshly boiled water to expel CO_2 . The solution was stored in a sealed plastic container initially purged with nitrogen gas (FEDGAS, high purity). This stock solution, as well as other solutions prepared from the stock solution, were standardized against potassium hydrogen phthalate [97].

2.3 Preparation and standardization of stock solutions of KELEX 100

The term 'active KELEX 100' refers specifically to the component 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline of the commercial KELEX 100 reagent supplied by SCHERING in Germany. The purity of the KELEX 100 reagent is estimated at 84-87% [98]. A pure sample of 'active KELEX 100' was unobtainable from Schering. Hence it was necessary to purify the crude commercial reagent.

2.3.1 Purification of crude KELEX 100

The crude sample of KELEX 100 was a clear viscous liquid and was amber in colour.

Boumezioud *et al.* [99] obtained pure KELEX 100 by using column chromatography and thin layer chromatography with hexane-ethylacetate in the ratio 80:20 (v/v) as the eluent. This method was attempted by previous workers in this laboratory but no satisfactory results were obtained [100].

Demopoulos and Distin [101] purified KELEX 100 by vacuum distilling the crude reagent at 140°C at a pressure of 0.02 mm Hg. A two component product was obtained consisting of 90% 'active KELEX 100'. Gareil *et al.* [102] also obtained high purity KELEX 100 by vacuum distillation in the range 170-180°C at a pressure of 0.5 mm Hg.

In this work it was decided to purify the KELEX 100 by vacuum distillation. The vacuum distillation apparatus is shown in Figure 2.1. The crude KELEX 100 (ca. 400 cm³) was poured in a 3-necked round-bottomed flask of 1 dm³ capacity. A 30 cm vacuum-jacketed

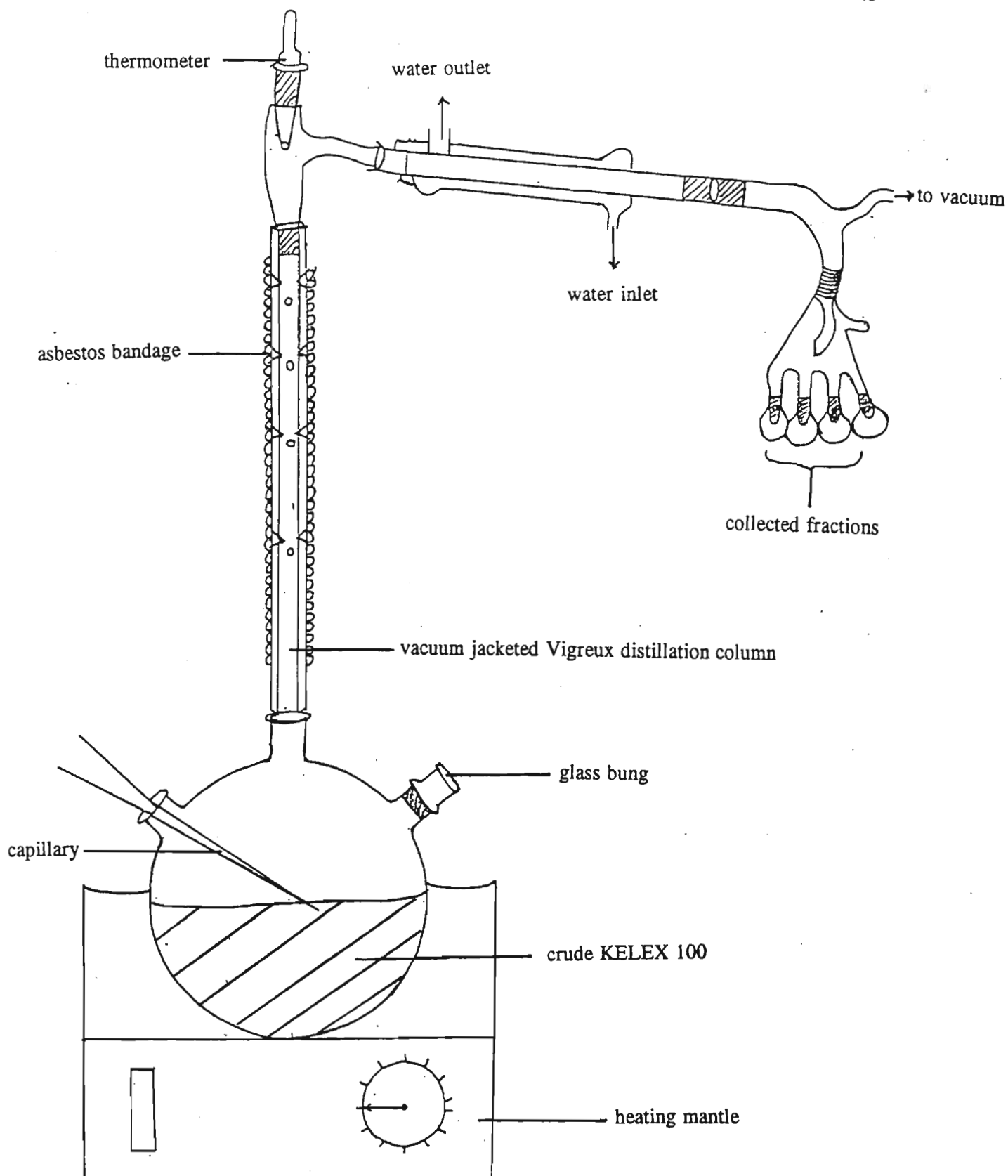


Figure 2.1 Vacuum distillation apparatus for the purification of crude KELEX 100.

Vigreux distillation column was attached. The column and the flask were insulated with aluminium foil and asbestos string to minimise heat loss. A glass capillary was used to introduce a fine stream of air bubbles to minimise 'bumping' [103]. A loose packing of glass wool was also placed above the liquid to minimise bumping [104]. An Edwards rotary vacuum pump was used to obtain a vacuum range of 0.2 - 0.3 mm Hg. KELEX 100 had been found previously to distil at 140°C at 0.02 mm Hg [101] and between 170 - 180°C at 0.5 mm Hg [102]. Thus it was expected that, at a vacuum of 0.2 - 0.3 mm Hg, KELEX 100 would distil in the range 140 -170°C. The vacuum distillation was carried out carefully to ensure that each fraction was collected in as narrow a temperature range as possible.

Eight samples were collected between 148°C and 158°C. Owing to the small size of the collection flasks, several samples which distilled at the same temperature were collected separately and should not be confused with different fractions, i.e. distillate which distils at different temperatures. Table 2.1 shows the conditions under which these samples were collected. Samples 3 and 4 were collected continuously and were regarded as one boiling fraction. Samples 5 and 6 are also regarded as a single fraction. Sample 7 was a small fraction of negligible mass and disregarded. Thus it is clear that five fractions were collected. These fractions varied in colour between light yellow and light brown. They were characterized by various analytical techniques to assess their purity.

2.3.2 Analytical techniques to assess the purity of each fraction

The five fractions as well as a sample of crude KELEX 100 were analyzed by thin layer chromatography. Samples were dissolved in methylene chloride (to improve the mobility) and spotted on MERCK t.l.c. plates (Kieselgel 60, t.l.c. aluminium plates, 0.2 mm thickness)

Table 2.1.

Results of the vacuum distillation of impure KELEX 100.

Sample number	Temperature/ °C	Pressure/ mmHg	Boiling fraction
1	148	0.2	A
2	150	0.2	B
3	152	0.2	C
4	152	0.2	C
5	156	0.3	D
6	156	0.3	D
7	158	0.3	-
8	184	0.3	E

1 cm from the edge. The plates were run in a t.l.c. chromatank containing sufficient solvent to cover 0.5 cm of the bottom edge of the plate. The solvent system used was carbon tetrachloride : methylene chloride in the ratio 95:5 (v/v). The plates were developed by spraying with a 0.05 M $\text{Al}_2(\text{SO}_4)_3$ solution and drying at 90°C.

The crude KELEX 100 separated into six spots, including two of fluorescent material. An example of a t.l.c. chromatogram is shown in Figure 2.2. The samples collected from the vacuum distillation separated into five distinct components (including the two fluorescent ones), indicating that the purification method was at least partially successful.

Mass spectra of each fraction were obtained by using a Hewlett-Packard 5890 SERIES II Gas Chromatograph coupled to a 5971 Mass Selective Detector. A 5% phenyl-methyl-silicone column of 0.25 μm thickness and a length of 30 m was used. Helium was used as the carrier gas. The samples were run isocratically at 150°C. Each of the five fractions were submitted for GC-MS analysis. Table 2.2 shows the amount of 'active KELEX 100' in each fraction. Fractions A, D and E were shown to have high concentrations of 'active KELEX 100' and were combined. This mixture was also submitted for GC-MS analysis and shown to contain 'active KELEX 100', of molar mass 299 g mol^{-1} , to be the major component at 94.30% of the total components analyzed. Three components of this mixture were separated on the gas chromatograph.

The mass spectrum of the purified KELEX 100 (see Figure 2.3) showed prominent peaks at the following m/e values: 299, 270, 242, 200, 173, 158, 57. These peaks compare favourably with the mass spectrum provided by Schering for 'active KELEX 100' [105].

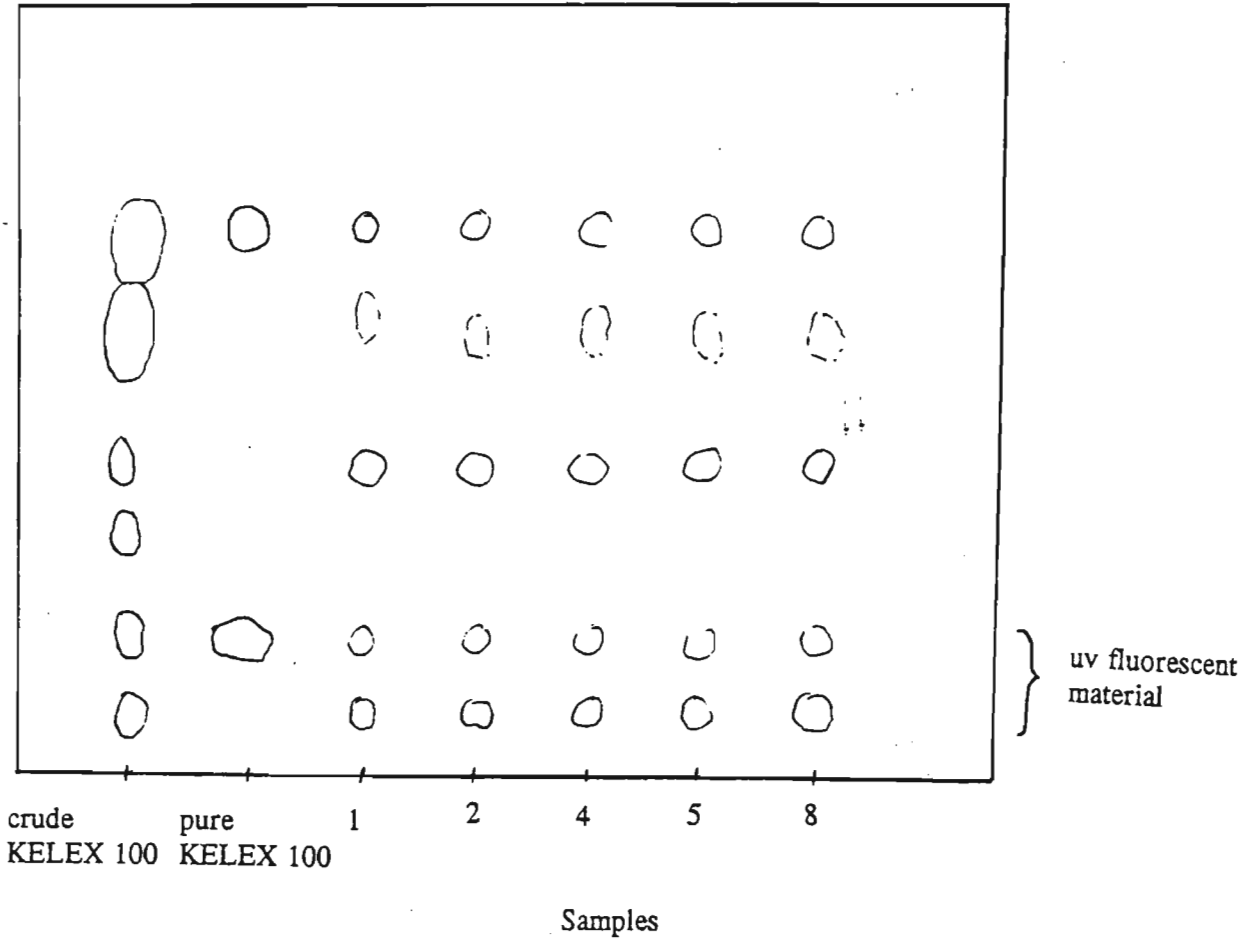


Figure 2.2 T.l.c. chromatogram showing the separation of each boiling fraction of crude KELEX 100 into several components.

Table 2.2

GC-MS analysis of 'active' KELEX 100 (in %) in each boiling fraction.

Boiling fraction	% 'active' KELEX 100
A	95.52
B	36.52
C	79.18
D	95.51
E	88.60

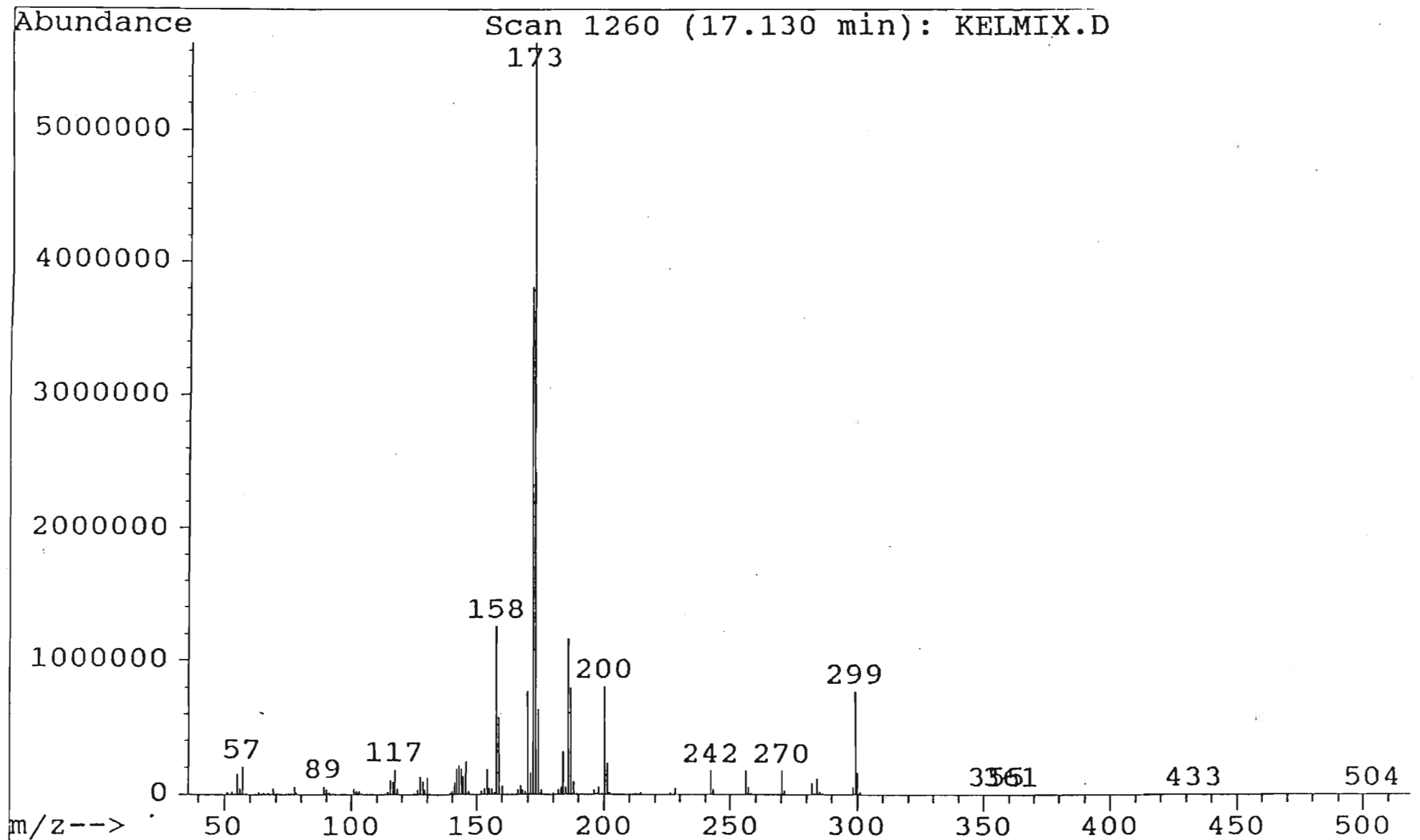


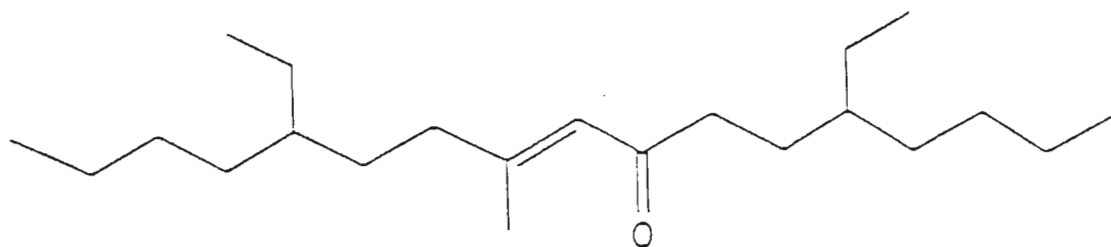
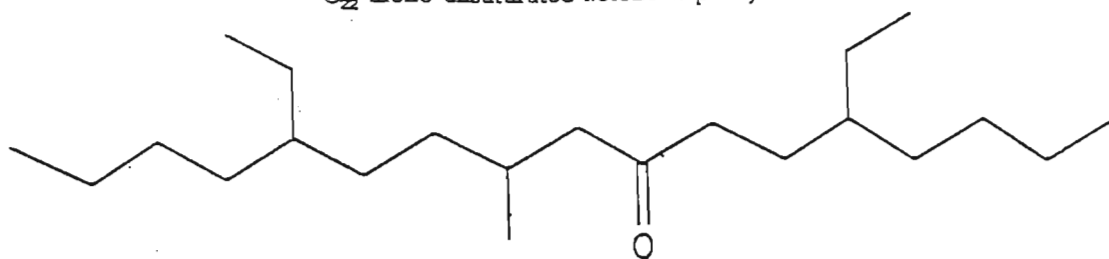
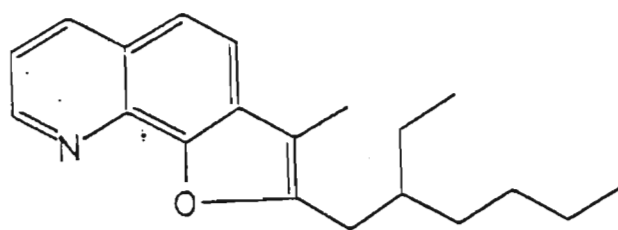
Figure 2.3 Mass spectrum of purified KELEX 100.

The remaining two components were identified by comparing their mass spectra to that of the mass spectra (provided by Schering) of the impurities in KELEX 100 [105]. According to Schering, the impurities in commercial KELEX 100 include a C_{22} ketone, a C_{22} mono-unsaturated ketone, a 5,7-disubstituted-8-hydroxyquinoline, a substituted furoquinoline and a substituted tetrahydrofuroquinoline. The structures of these impurities are shown in Figure 2.4.

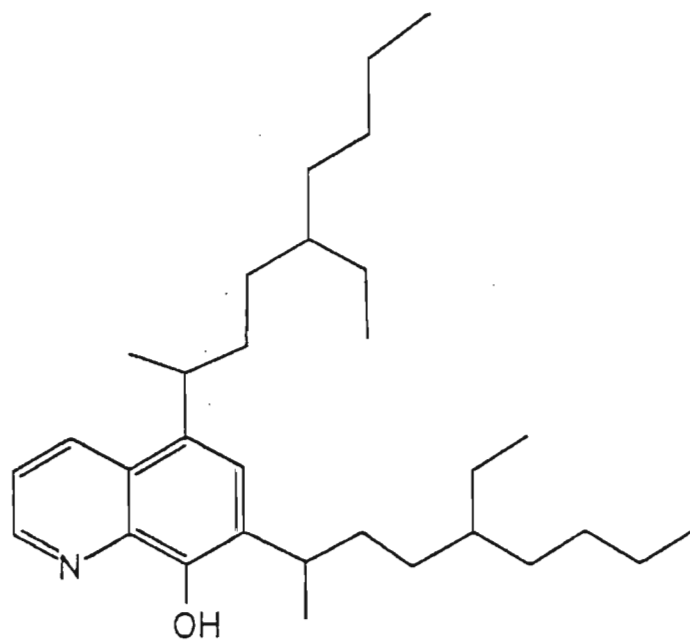
The molar masses of the remaining components were 295 g mol^{-1} and 324 g mol^{-1} . The former component (Figure 2.5) showed prominent peaks at the following m/e values : 266, 238 and 196. This was identified as the alkylated furoquinoline. This impurity made up 4.30% of the total components analyzed. According to Demopoulos and Distin [101], the furoquinoline derivatives lack the complexing properties of 8-hydroxyquinolines.

The mass spectrum of the remaining component (Figure 2.6) showed prominent peaks at the following m/e values : 295, 248, 207, 183, 155 and 57. This was shown to be the C_{22} ketone, $C_{22}H_{44}O$. It is unlikely that this component would have chelating properties since it has a single oxygen atom with lone pairs available for bonding. The oxygen atom is also sterically hindered by the β -methyl group. Due to the non-complexing nature of the impurities, these were not believed to contribute to any significant error in subsequent experiments. None of the other impurities reported by Schering were observed.

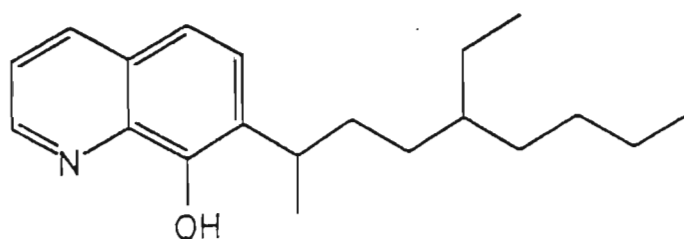
A nmr spectrum of purified KELEX 100 made up in deuterated chloroform was recorded on a Varian Gemini 300 nmr spectrometer. The spectrum and the structure of KELEX 100 with the differently labelled protons is shown in Fig 2.7. Nmr spectra for pre-1976 KELEX 100 have been reported in the literature [106]. For post-1976 KELEX 100, however, the only

C₂₂-mono-unsaturated ketone impurityC₂₂-ketone impurity

alkylated furoquinoline impurity



5,7-disubstituted-8-hydroxyquinoline impurity



'active' KELEX 100

Figure 2.4 The structures of the impurities and 'active' KELEX 100 reported by Schering.

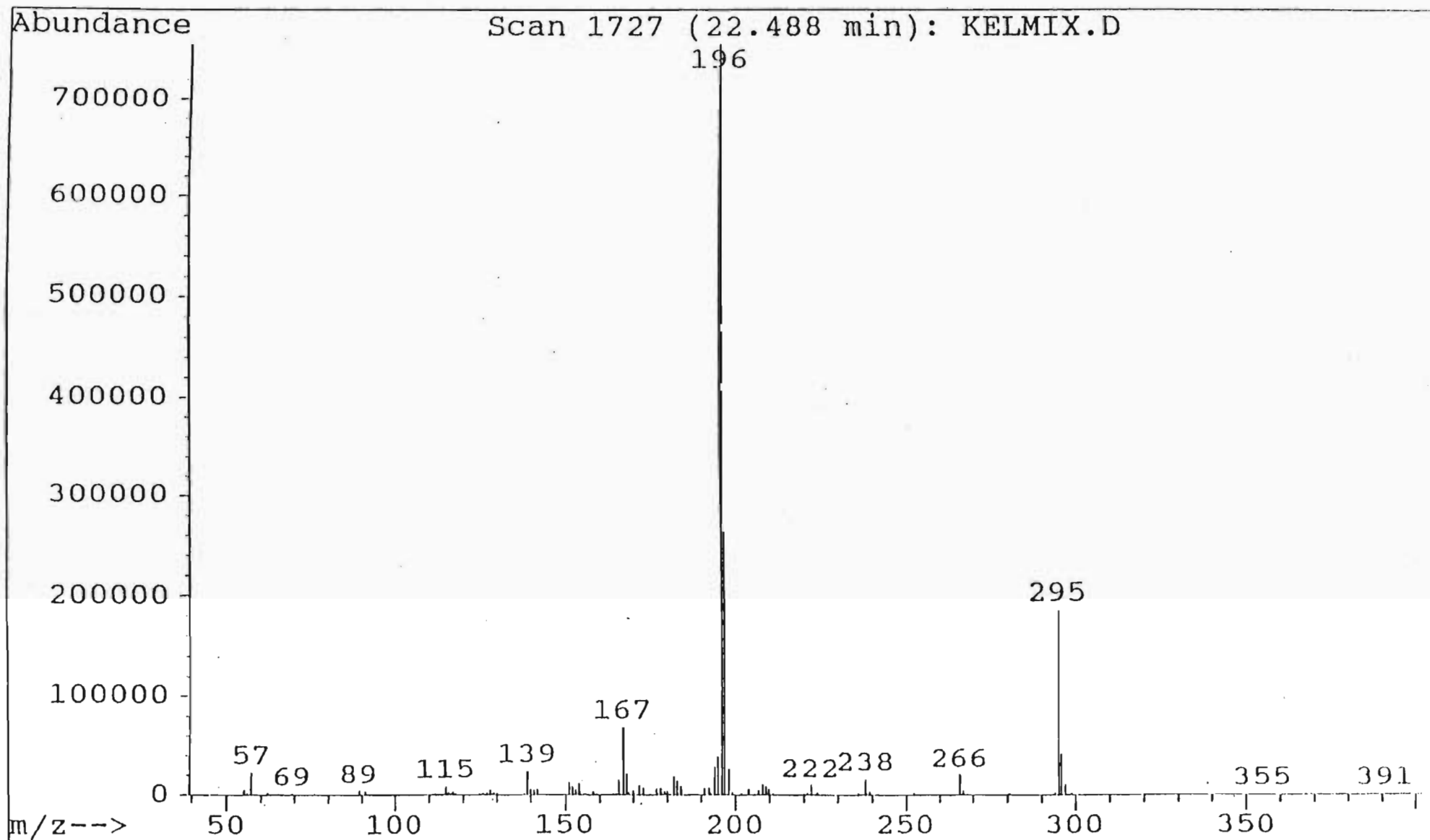


Figure 2.5 Mass spectrum of the alkylated furazquinoline impurity

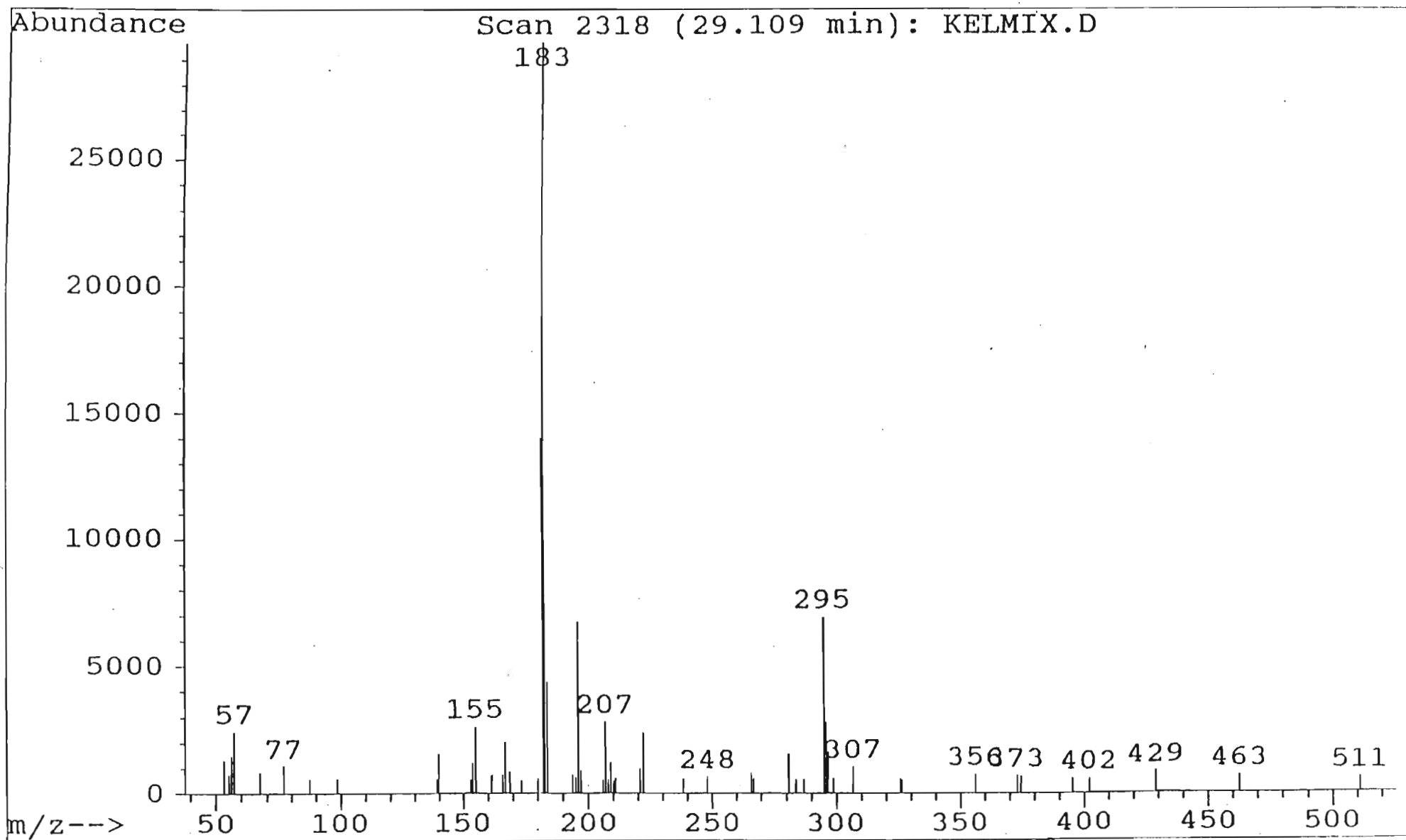
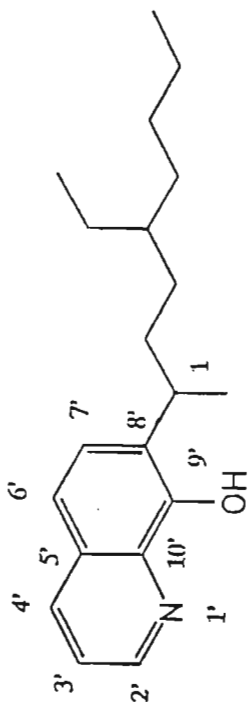


Figure 2.6 Mass spectrum of the C₂₂-ketone impurity.



HK100.KELEX-100 IN CDCL3

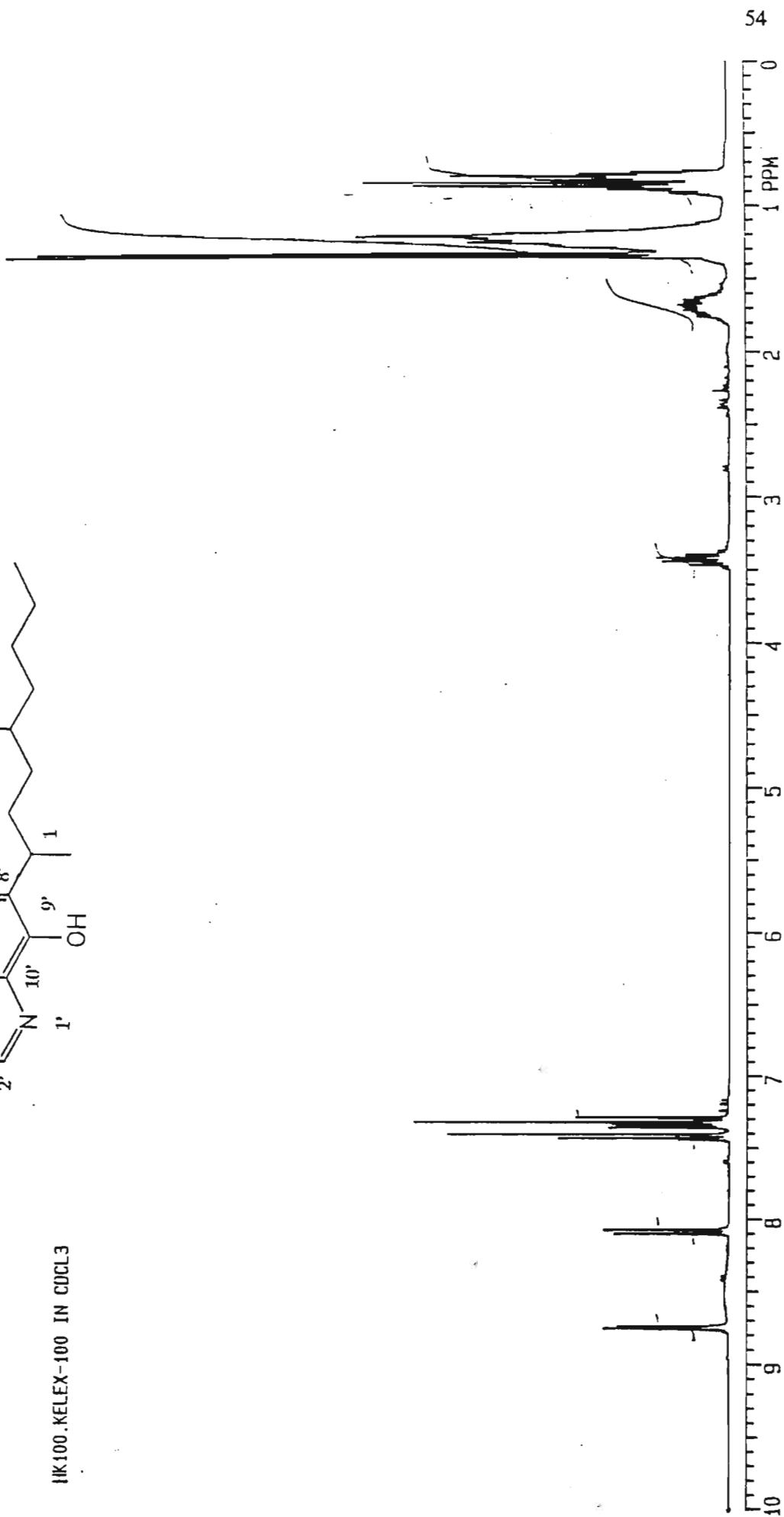


Figure 2.7 Nmr spectrum of purified KELEX 100.

nmr spectrum available for comparison was reported by a previous worker in this laboratory [107]. The nmr spectrum obtained in this work is almost identical to the reported spectrum (shown in Figure 2.8).

The chemical shifts (δ) in ppm for the different protons in the KELEX 100 molecule were found to be:

- (i) Proton 2' as a doublet at 8.74 ppm
- (ii) Proton 7' as a doublet at 8.10 ppm
- (iii) Proton 3' as a doublet of doublets, proton 6' and proton 4' as doublets in the range 7.25-7.50 ppm
- (iv) The hydroxyl group at 3.42 ppm

The three methyl groups were found in the range 0.76-0.93 ppm. The methyl group at C-1 should be shifted downfield due to the inductive effect of the hydroxyl group. The six methylene groups were found between 1.11 and 1.35 ppm, while the two methine groups appeared between 1.60 and 1.76 ppm.

2.3.3 Preparation and standardization of KELEX 100 stock solutions

Stock solutions of KELEX 100 (ca. 0.2 mol dm⁻³) were prepared from the combined distillation fractions with the highest percent purity of KELEX 100 and made up in 1,4-dioxane. The stock solution could not be standardized by potentiometric titration against standard strong base since no sharp equivalence point was observed from the plots of e.m.f. versus volume of titrant added [107,108]. Previous workers in this laboratory [107,108] adapted a method that Campbell *et al.* [109] used to standardize bithiosemicarbazones. This

HK100.KELEX 100 IN CDCL3

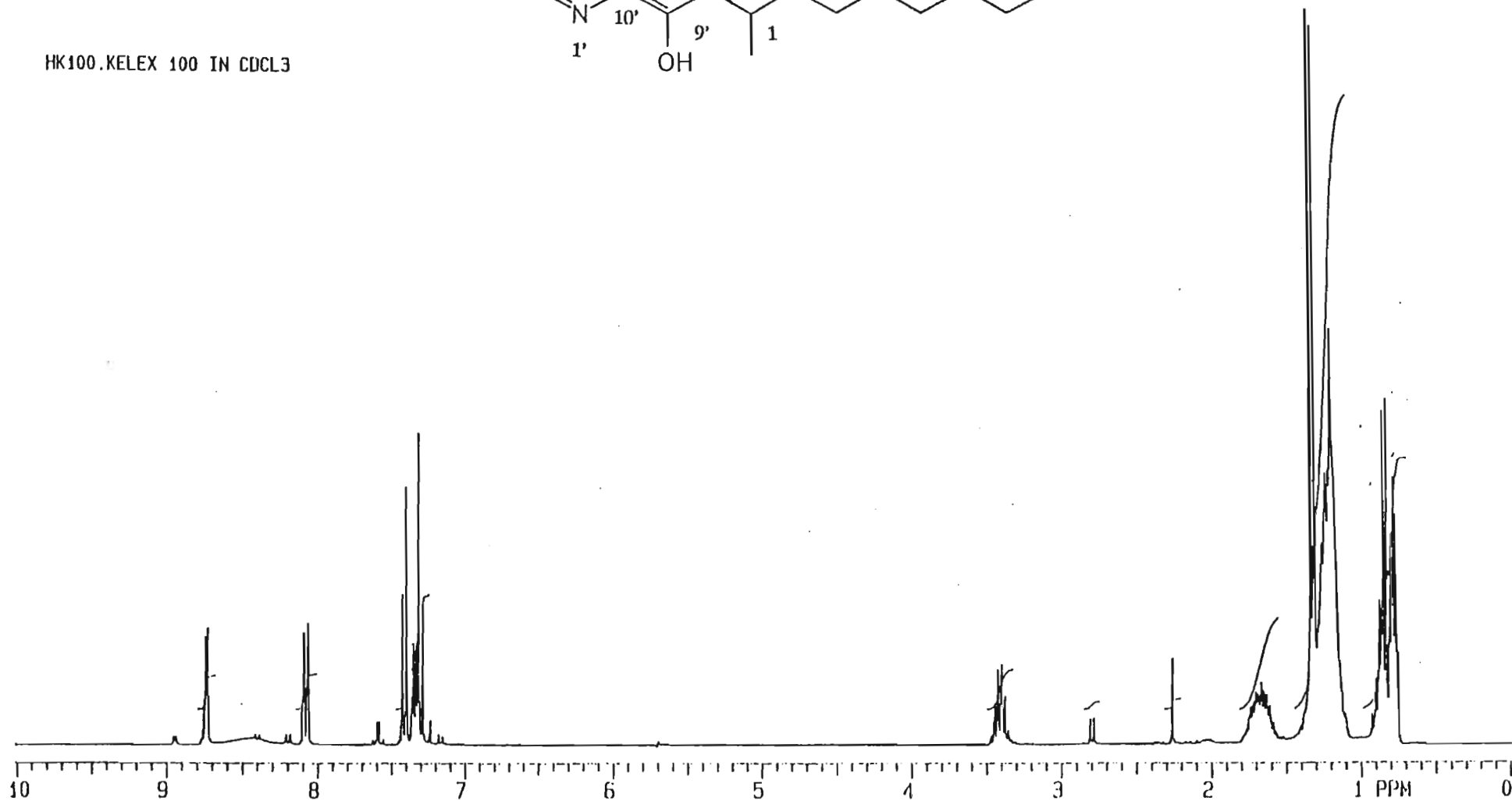
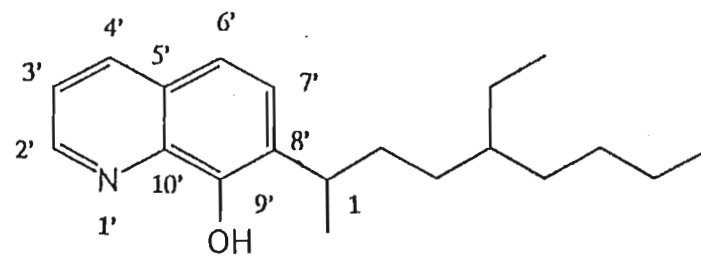


Figure 2.8 Nmr spectrum of purified KELEX 100 obtained by Lee [107].

method involved the addition of sufficient $\text{Cu}(\text{NO}_3)_2$ solution to an aliquot of KELEX 100 so that only the Cu-KELEX 100 complex would form. The hydrogen ions liberated on the formation of this complex were titrated potentiometrically against standard sodium hydroxide.

There are two disadvantages to this method:

- (i) In the vicinity of the endpoint, the excess hydroxide reacts with the Cu-KELEX 100 complex to form a $\text{Cu}(\text{OH})_2$ precipitate. The presence of these solids may influence the response of the electrode.
- (ii) The titration is carried out by titrating an aqueous titrant into a non-aqueous titrate. The effect of this on the electrode response is not known.

A preferred method of standardizing the KELEX 100 is to potentiometrically titrate it against HClO_4 , both solutions being made up in 1,4-dioxane [110]. The HClO_4 solution is first standardized potentiometrically against recrystallised borax and then titrated into a solution of KELEX 100 in dioxane. Data for such a titration is given in Table 2.3. A plot of e.m.f. versus volume of acid added (Fig. 2.9) produced a curve with an equivalence point which could be determined by construction. For the example given, the endpoint occurred at 20.31 cm^3 and thus the KELEX 100 concentration was $0.1968 \text{ mol dm}^{-3}$.

2.4 Preparation and standardization of stock solutions of metal ions

2.4.1 Preparation and standardization of stock solutions of lead perchlorate

A stock solution of lead perchlorate (ca. 0.5 mol dm^{-3}) was prepared by dissolving SAARCHEM PbO (min. 99% pure) in sufficient KLEBER HClO_4 (min. 70% pure, sp. gr.

Table 2.3

Data for the standardization of ca. 0.2 mol dm^{-3} KELEX 100 solution (in dioxane) against standard $0.0969 \text{ mol dm}^{-3}$ HClO_4 (in dioxane). A volume of 10.00 cm^3 of KELEX 100 was used.

Volume of titrant added/ cm^3	emf/mV
15.00	-278
15.50	-281
16.00	-284
16.50	-287
17.00	-290
17.50	-294
18.00	-298
18.50	-303
19.00	-310
19.50	-320
19.70	-325
20.00	-334
20.10	-340
20.20	-346
20.30	-353
20.40	-362
20.50	-366
20.60	-370
20.70	-373
20.80	-372
20.90	-372
21.00	-372
21.10	-371
21.20	-370
21.30	-370
21.40	-369
21.50	-369

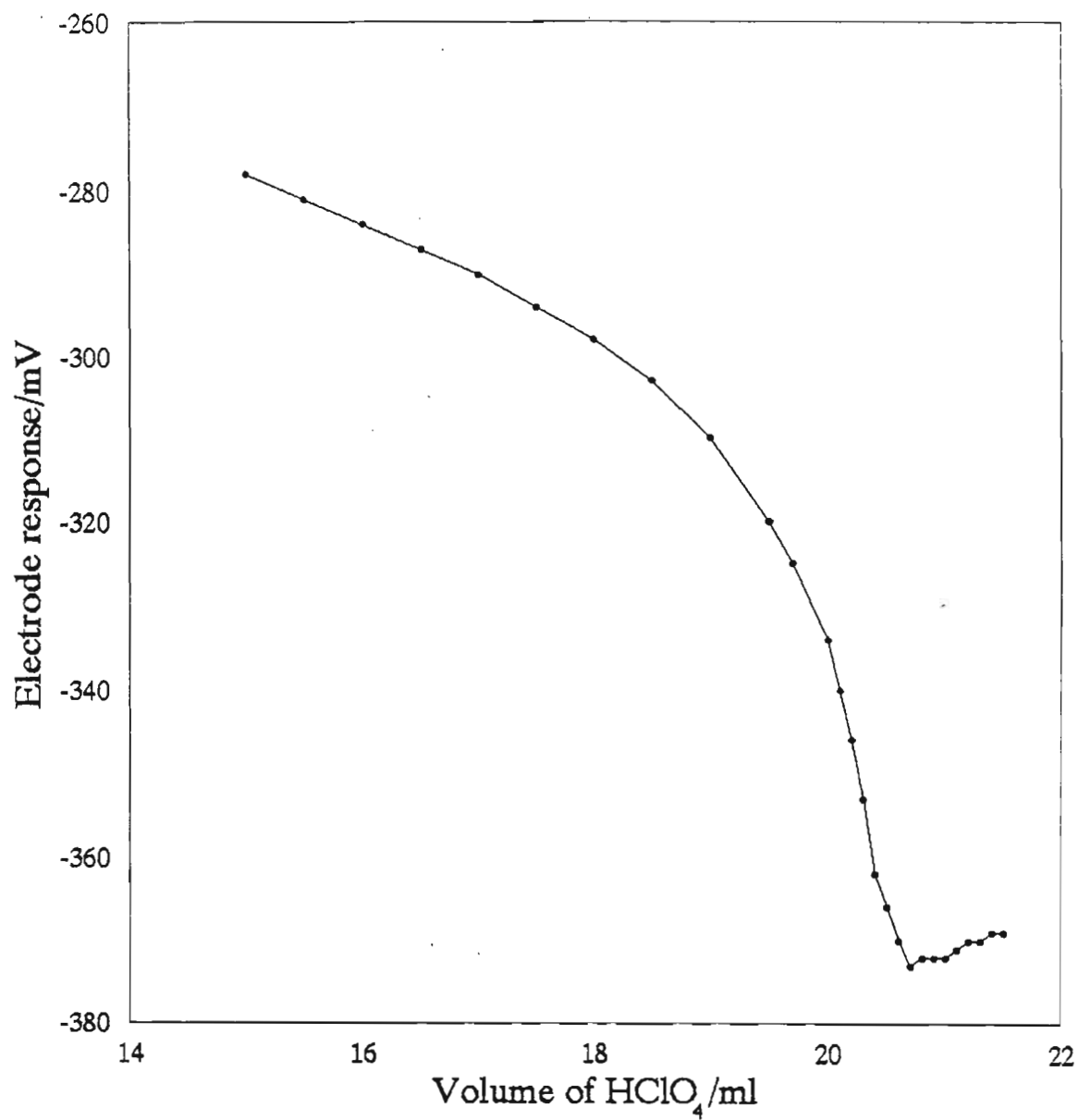


Figure 2.9 Potentiometric titration curve for the standardization of KELEX 100 against HClO₄ in dioxane.

1.67) and ca. 150 cm³ water. The solution was filtered through Whatman No. 1 filter paper to remove undissolved impurities and made up with water.

The stock solution was standardized by titration against a 0.05 mol dm⁻³ standard EDTA solution (BDH, min. 98% pure) in the presence of hexamine with xylenol orange as indicator [111]. The EDTA was recrystallised before preparation of the standard EDTA solution [112]. For the standardization, a ca. 0.05 mol dm⁻³ Pb(ClO₄)₂ solution was used.

The concentration of the excess acid present in the lead perchlorate solution was determined by titration against freshly prepared standard sodium hydroxide solution, using phenolphthalein as indicator. An aliquot of HClO₄ was added to the Pb(ClO₄)₂ solution to facilitate the detection of the endpoint. The concentration of the excess acid was found to be 0.0665 mol dm⁻³ HClO₄.

2.4.2 Preparation and standardization of stock solutions of cadmium nitrate

A stock solution of cadmium nitrate (ca. 0.15 mol dm⁻³) was prepared from Merck Cd(NO₃)₂·4H₂O (min. 99% pure) and made up with water.

The stock solution was standardized by titration against a 0.05 mol dm⁻³ standard EDTA solution (BDH, min. 98% pure) in the presence of hexamine with xylenol orange as indicator [111]. The EDTA was recrystallised before preparation of the standard EDTA solution [112]. For the standardization, a ca. 0.05 mol dm⁻³ Cd(NO₃)₂ solution was used.

2.4.3 Preparation and standardization of stock solutions of nickel nitrate

A stock solution of nickel nitrate (ca. 0.2 mol dm^{-3}) was prepared from Merck $\text{Ni}(\text{NO}_3)_2$ (min 99%).

The stock solution was standardized by titration against a 0.05 mol dm^{-3} standard EDTA solution (BDH, min. 98% pure) in the presence of an aqueous $\text{NH}_4\text{Cl}/\text{NH}_3$ buffer (0.1 mol dm^{-3})

using bromopyrogallol red as indicator [111]. The EDTA was recrystallised before preparation of the standard EDTA solution [112]. A ca. 0.01 mol dm^{-3} $\text{Ni}(\text{NO}_3)_2$ solution was used for the standardization.

2.5 Purification of 1,4-dioxane

The 1,4-dioxane used was obtained from Janssen Chemicals (99+ % pure, stabilized with 25 ppm 2,6-di-tert-butyl-p-cresol). The main impurity was glycol acetal which undergoes hydrolysis to liberate acetaldehyde which in turn leads to peroxide formation. Vogel suggests decomposition of the acetal with acid, drying and then fractionating [113].

A volume of 1 dm^3 of 1,4-dioxane, 14 cm^3 of BDH hydrochloric acid (min. 33% pure, sp. gr. 1.16) and 100 cm^3 of water were added to a round-bottomed flask of 2 dm^3 capacity. The solution was refluxed for 6 hours to remove the acetaldehyde [113]. The solution, which was slightly discoloured, was cooled and laboratory grade potassium hydroxide (KOH) pellets (ca. 150 g) were added. The solution was magnetically stirred until all the potassium hydroxide had completely dissolved. The aqueous layer was removed with a separating funnel. Fresh

KOH pellets (about 80 g) were added to the solution until some remained undissolved after stirring. The aqueous layer was again separated from the clear 1,4-dioxane solution which was allowed to stand overnight over fresh KOH pellets (ca. 20 g) to remove all residual water. The solvent was removed from the KOH pellets by careful decantation and refluxed over sodium metal lumps for at least 6 hours. The 1,4-dioxane was distilled from sodium at 101°C and stored in stoppered conical flask over MERCK molecular sieve (sodium aluminosilicate type 4A pellets).

The moisture content of purified and unpurified 1,4-dioxane was determined by the Karl Fisher method using a Mettler automatic 701KF Titrino system. Samples of at least 0.5 g mass was necessary to ensure reproducible results. Typical moisture contents for purified 1,4-dioxane were 0.02% This compares well with a value of 0.14% obtained by Edwards [108].

CHAPTER THREE

APPARATUS

The calorimeter and associated equipment used in this work to determine enthalpy changes are described in this chapter. The techniques used to calibrate the components of the calorimetry system are also described.

3.1 Description of the calorimeter

Enthalpy changes were measured with an LKB 2107 Microcalorimetry system which consists of a LKB 2107 Microcalorimeter, an LKB 2107/210 thermostat and an LKB 2107 Control Unit. A Perkin-Elmer 561 strip chart recorder was used to record the output. There are two types of cells that can be used with the microcalorimeter, viz.

- (i) a flow-mix cell - used to measure the heat of mixing between two solutions,
and
- (ii) a flow-through cell - used to measure heat evolved in a solution when the reactants have been pre-mixed.

The flow-mix cell was used in this work. A schematic diagram of the calorimetry system is shown in Figure 3.1.

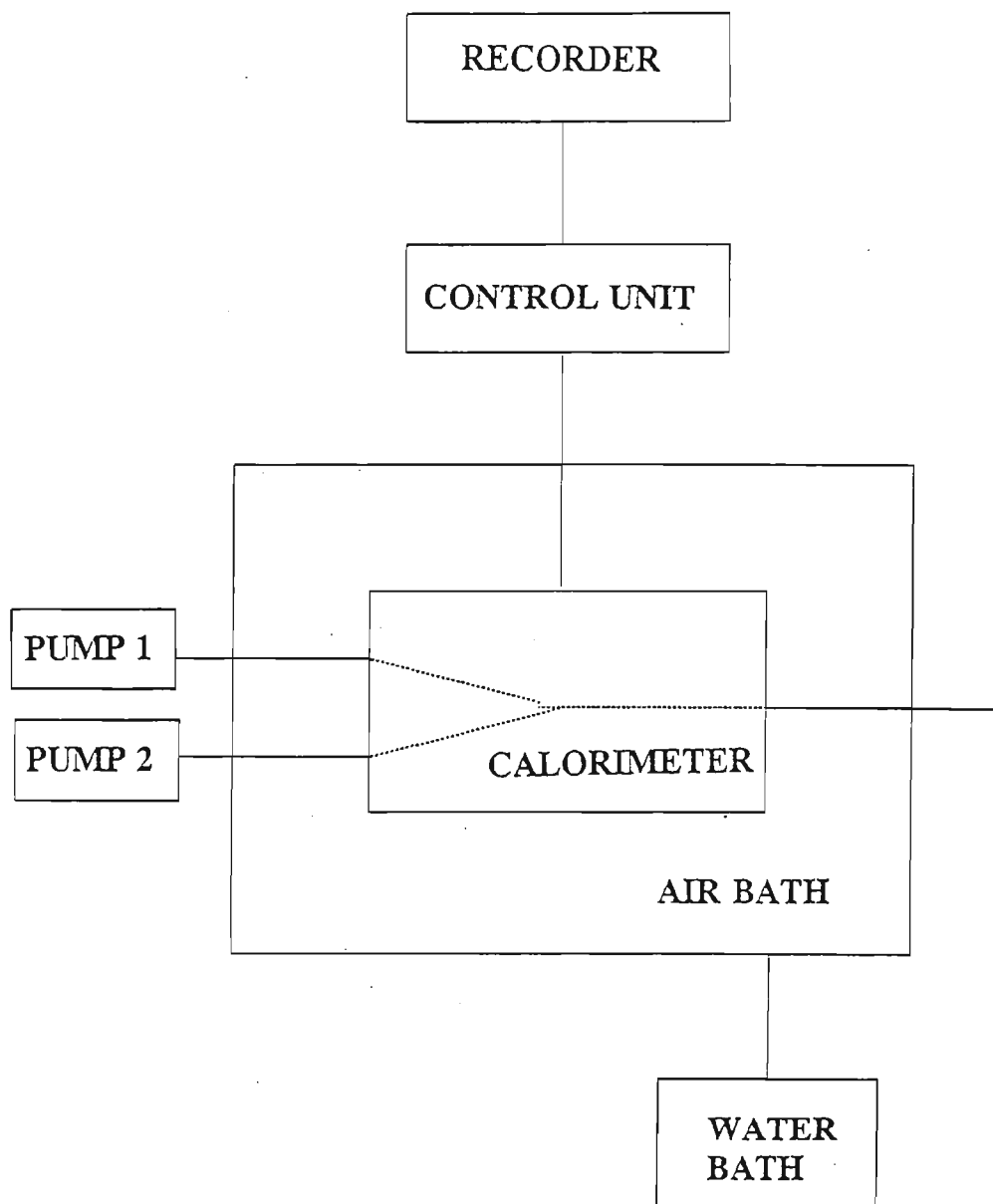


Figure 3.1 Schematic diagram of the LKB Flow Microcalorimetry system.

3.2 Principle of operation

The microcalorimeter is fitted with two separate vessels in which reactions can take place. Each vessel is in thermal contact with a pair of thermocouples and an aluminium heat sink assembly. The microcalorimeter is a heat conduction type calorimeter which is designed on the heat leakage principle, i.e. if heat is generated by the reaction (exothermic) in a vessel, then heat flows from the vessel to the heat sink assembly. For endothermic reactions, heat flows from the heat sink to the vessel. Thermopiles (temperature sensors) are located between the vessels and the heat sink assembly and the temperature difference creates a heat flow across them which gives rise to an emf which is proportional to the temperature difference. This output voltage from the thermopiles is amplified and fed into a recorder. The calorimeter can be electrically calibrated with a built-in heater and the output used to determine the heat effect [114]. In practice, only part of the vessel is covered by the thermopiles and a significant proportion, typically 20 percent or more, of the heat evolved in the vessel will leak to the surroundings via air gaps, electrical leads and mechanical supports. This does not give rise to any systematic errors provided the calibration of the calorimeter is performed properly [115].

To ensure the stable temperature environment necessary for calorimetric experiments, the microcalorimeter is placed in a thermostatically controlled air bath which was maintained at a temperature of 25.000 ± 0.004 °C. The bath is made of stainless steel with a loose lid fitted to the top. Both the bath and the lid are insulated with plastic foam. A blower circulates air in the bath and a 50 W heater is used in conjunction with a control circuit to control the temperature [116]. It was also necessary to install an external cooling unit (a Labcon low temperature water bath with circulator) as an external heat exchanger to efficiently remove

heat when working at temperatures below 25°C. The temperature in the thermostat was measured with a 2804A Hewlett Packard Quartz thermometer fitted with a HP18110A temperature probe.

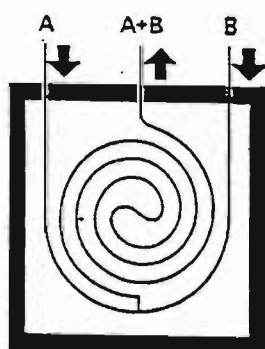
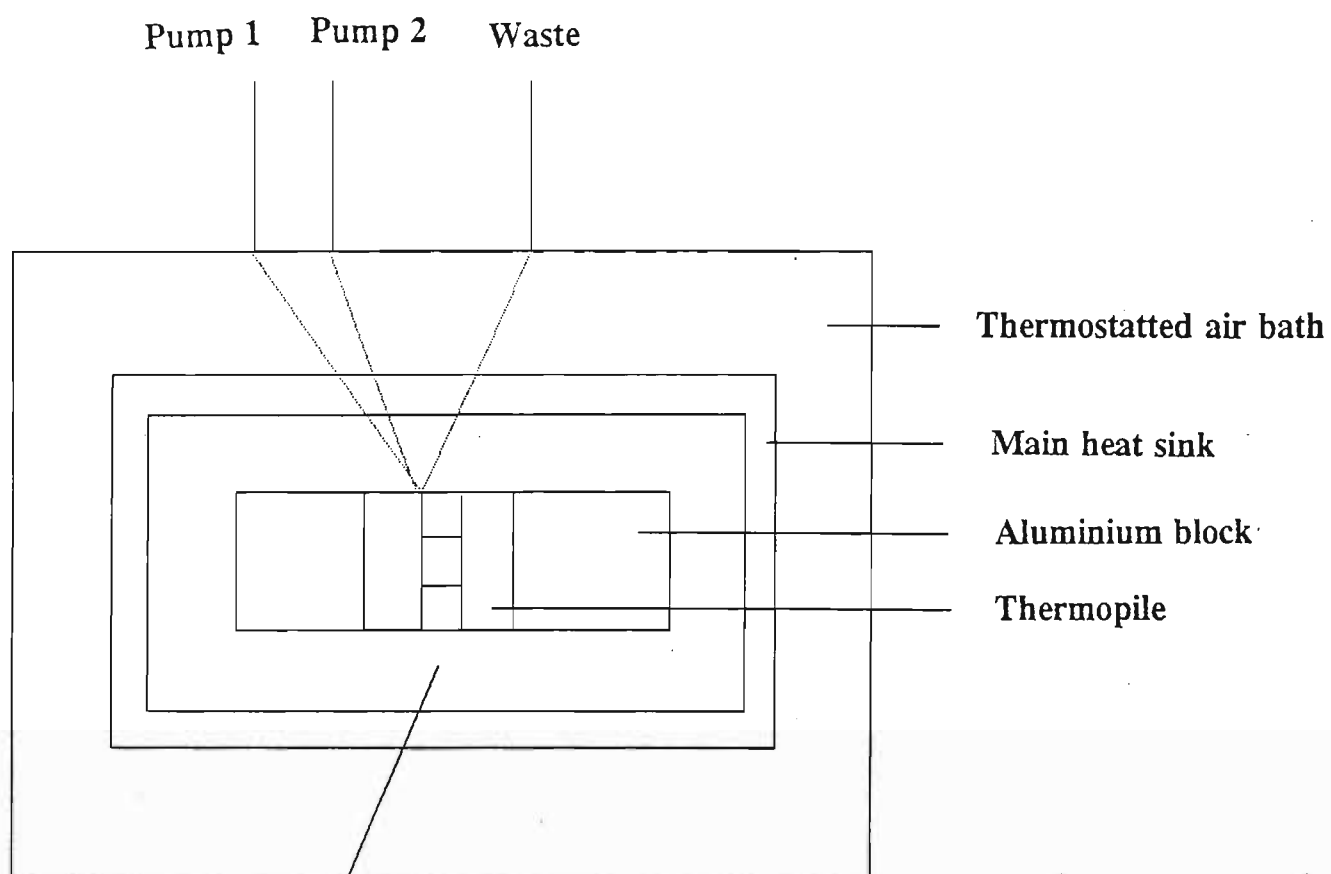
The two reactant solutions are pumped separately via Perpex peristaltic pumps into the mixing cell where they are thoroughly mixed. The reacted mixture leaves the mixing cell via an outlet tube. It is necessary for the reactants flowing in the calorimeter to be within 0.05°C of the operating temperature of the calorimeter in order to reach thermal equilibration quickly prior to entering the mixing cell. The liquids were routed through an external heat exchanger (fitted in the recess of the thermostat) prior to entering the mixing vessel to ensure that they were thermally equilibrated at the thermostat temperature. Figure 3.2. shows the internal representation of the heat sink assembly.

3.3 Electrical calibration of the calorimeter

The calorimeter is electrically calibrated by passing a known electrical current through the built-in heater located by the mixing cell for a known time. The current is derived from the control unit and the power generated is calculated using the known resistance of the calibration heater (which has a negligible temperature coefficient). The power (P_c) is given by:

$$P_c = I^2R \quad (3.1)$$

where I is the current and R is the resistance of the calibration heater.



Flow-mix reaction cell

Figure 3.2 Internal representation of the heat sink assembly.

The magnitude of the recorder deflection, D_c , is in arbitrary units of length; in this work, millimetres. The calibration constant, ϵ , is then given by:

$$\epsilon = \frac{P_c}{D_c} \quad (3.2)$$

The heat effect, W_{exp} , of a particular reaction is obtained simply by multiplying the resultant recorder deflection, D_{exp} , by the calibration constant, i.e.

$$W_{\text{exp}} = D_{\text{exp}} \epsilon. \quad (3.3)$$

Electrical calibration was carried out before each experiment and at least once a day.

3.4 Calibration of peristaltic pumps

Solutions are pumped into the mixing cells via two Perpex peristaltic pumps. It was desired that both pumps should deliver the same volumetric flow rate. The pumps are designed to deliver flow rates up to 210 ml hr⁻¹ if water is pumped through. The calibration of the pumps entails pumping a liquid for a fixed time and, by difference, measuring the mass delivered. The masses are converted to volumes by measuring the density of the solution (described in Section 6.6). Attempts to construct calibration curves relating settings on the pump to flow rates were successful only at flow rates of about 20 ml hr⁻¹ since the pumps failed to deliver consistent volumes at lower flow rates (see Figure 3.3). However, the maximum flow rate permissible through the calorimeter mixing cell is 40 ml hr⁻¹ and hence only 20 ml hr⁻¹ per pump. It was eventually decided that these calibration curves would be unreliable and the

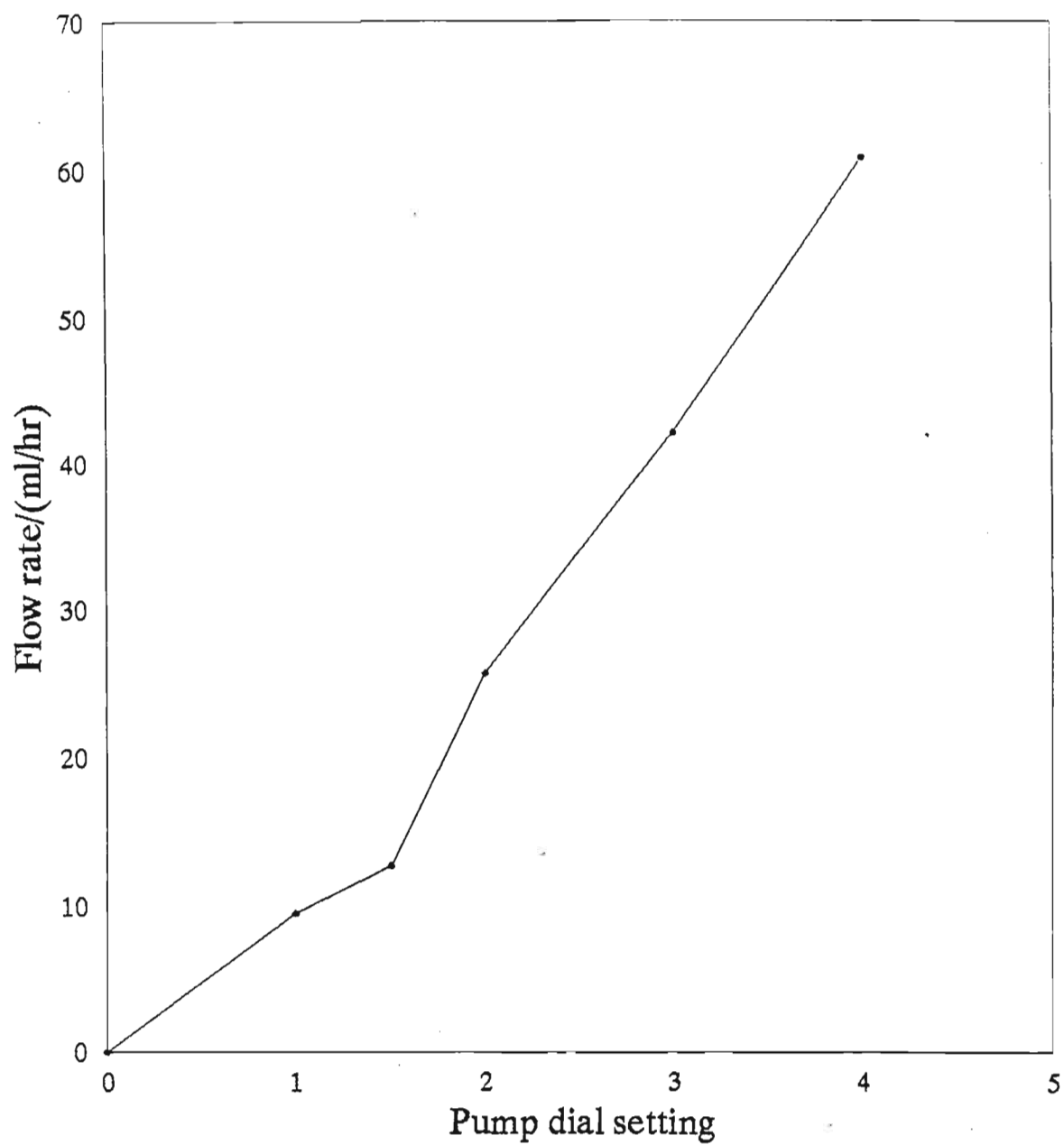


Figure 3.3 Calibration curve for the Perpex peristaltic pump.

settings of each pump would be kept approximately equal. Depending on the masses of solution delivered by each pump, the settings would be appropriately adjusted, by experience, to deliver similar flow rates. The inherent disadvantage of peristaltic pumps is that they produce a pulsed flow [117].

3.5 Calibration of the recorder

Appropriate scales on the recorder were chosen by reacting a pair of solutions expected to produce the maximum heat effect from a metal ion - KELEX 100 system, viz. the most concentrated metal ion solution was reacted with the standard deprotonated ligand solution. The scales were chosen for maximum sensitivity without sacrificing baseline stability. The value of the calibration current was selected so that the electrical calibration curve was easily accommodated on this scale and was similar in magnitude to the expected heat effect of the reaction between the metal ion and the ligand.

3.6 Calibration of the thermostat and water bath

The calorimeter temperature is stabilised by a control circuit which activates a 50 W heater and blower in an air bath thermostat. However, if the desired calorimeter temperature is near or below room (or ambient) temperature (typically 22°C), it is necessary to have an efficient external heat exchanger in the form of a water bath to quickly remove heat from the thermostat. It follows that the temperature of the water bath must necessarily be below that of the calorimeter temperature. The optimum operation of the water bath is essential to the stability of the calorimeter temperature. Specifications in the appropriate instrument manuals [114,116] were followed faithfully but the temperature fluctuated intermittently depending on

the room temperature. It was later discovered that the calorimeter was reconstructed following extensive previous damage and hence the settings on the calorimeter thermostat and water bath were changed by trial and error until the temperature stabilised and was independent of room temperature. The setting on the thermostat control knob was 498.5 and the water bath was set at 15°C to ensure the calorimeter temperature was stable at 25.00°C. This was an extremely time-consuming exercise since the calorimeter must be allowed to stabilise for at least 6 hours to determine the effect of each pair of settings. Further, it was found that scale formation in the connecting water hoses constricted the flow of water and heat exchange efficiency was diminished. Removing the scale in the connecting hoses and replacing the water in the bath periodically with fresh water solved this problem.

3.7 Description of special dispensing flasks

Reactant solutions are pumped into the calorimeter and allowed to react in the reaction cell. The solutions could be kept in any storage container, e.g. a beaker or a volumetric flask. However, it is necessary that the surface area of solution exposed to the atmosphere is kept to a minimum so as to reduce the rate of loss by evaporation. It was also desirable to make provision for a stream of inert gas, viz. nitrogen, to pass over the solution since the oxygen and carbon dioxide in air could be adsorbed, especially in the case of NaOH solutions. To achieve this, a set of specially designed flasks were made. A typical flask is shown in Figure 3.4.

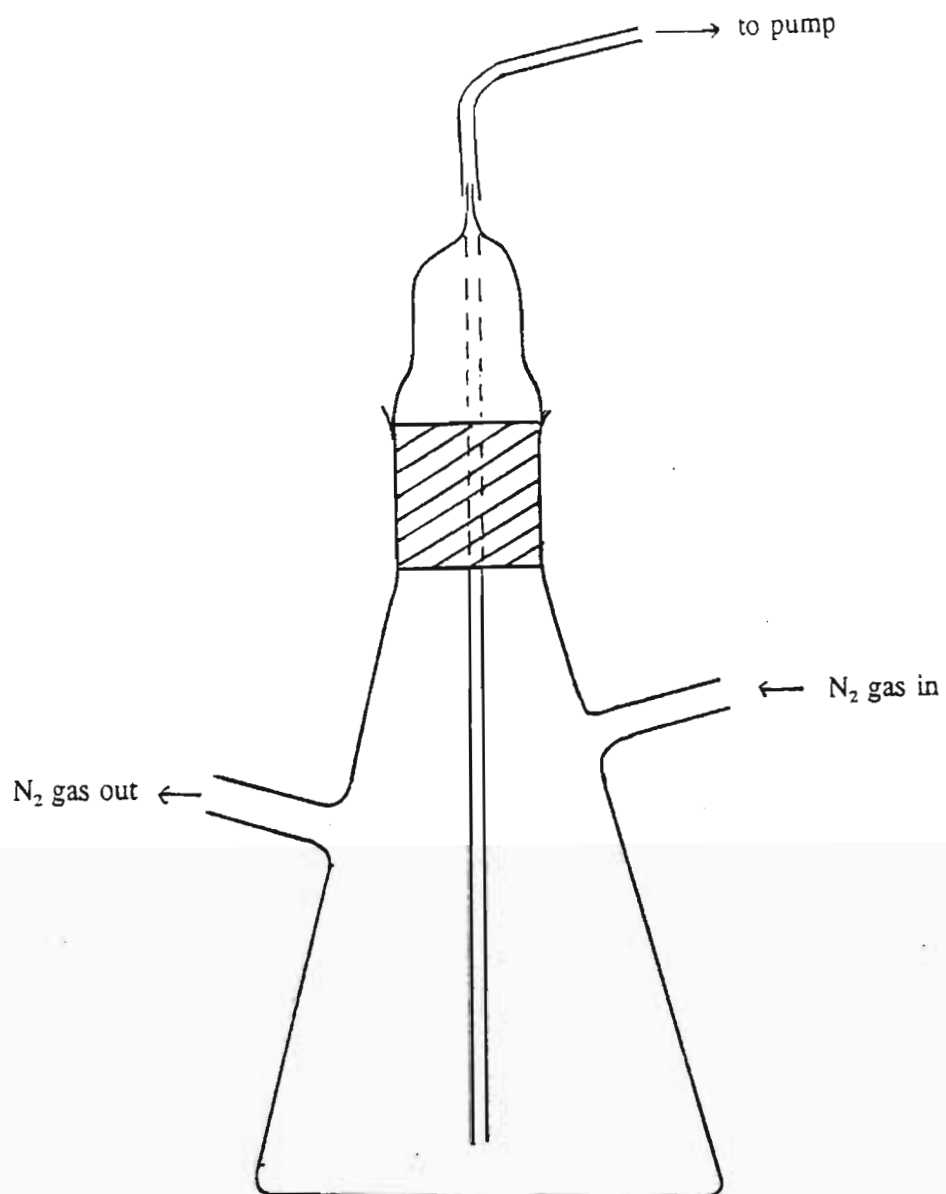


Figure 3.4 Special flasks used to dispense reactant solutions into the calorimeter.

CHAPTER FOUR

CALIBRATION OF THE CALORIMETER

Although the calorimeter can be calibrated electrically to determine the heat effect of a particular reaction, this can also give rise to systematic errors, viz. evaporation and condensation effects, heat leakage from the heater and localised heating dependent on the position of the calibration heater in the reaction cell [118]. It is necessary to identify these errors by performing a test reaction, preferably one that resembles the reaction of interest in terms of the sign and magnitude of the heat effect, and the kinetics and nature of the reaction. This is most conveniently done by chemically calibrating the calorimeter by measuring the enthalpy change of a well-studied reaction for the which the enthalpy change is accurately known. In this work the calorimeter was calibrated using an aqueous test reaction.

4.1 Choice of test reaction

Several test reactions have been proposed for use as chemical calibration standards, notably the dissolution of KCl in water [119], the enthalpy of protonation of tris(hydroxymethyl)aminomethane, better known as TRIS or THAM [118] and the classical neutralization of a strong monobase with a strong monoacid. The dissolution of KCl in water was found to be unsuitable because the reaction had a low endothermic enthalpy and the method of preparation and purification also led to different values being obtained [120]. The reaction of TRIS with HCl has been shown to be a convenient standard, provided the TRIS

crystals are dried carefully to nullify the effects of mechanical strain in its preparation [121]. A comparison of the TRIS protonation and the heat of neutralization between a strong acid and strong base shows that both are as accurate but that the latter reaction is probably better due to the effect of adsorbed CO_2 which has no effect on the heat of neutralization [122]. Also, the use of perchloric acid, HClO_4 , is preferred to hydrochloric acid, HCl , due to the large enthalpy of dilution of HCl . Sodium hydroxide (NaOH) is usually used as the monobase. There is no universally accepted chemical test reaction for calorimetry although there are still test reactions that are being proposed such as the more recent reaction of the protonation of 4-aminopyridine in aqueous HClO_4 [123]. Further refinements of well-known test reactions also claim particular advantages as does the recent investigation of the protonation of TRIS [124]. In this work, the test reaction chosen for chemical calibration of the calorimeter was the heat of neutralization of a strong acid (HClO_4) with a strong base (NaOH). This was preferred since it was envisaged that the heat of neutralization in a mixed 1,4-dioxane-water solution would also have to be determined for use in the determination of the enthalpies of complexation. The experience gained in performing the calibration by using the aqueous heat of neutralization reaction could then easily be extended to the determination of the heat of neutralization in the 1,4-dioxane-water solvent system used for the rest of the measurements.

4.2 Outline of experimental procedure

All reagents were made up in aqueous solution.

A stock HClO_4 solution (0.01 mol dm^{-3}) was used as the "titrate" solution. Twelve "titrant" solutions of NaOH were made up in concentrations varying from $0.0050 \text{ mol dm}^{-3}$ to 0.0105

mol dm⁻³, in intervals of 0.0050 mol dm⁻³. All solutions were made up to 0.1 mol dm⁻³ ionic strength using NaClO₄. Each of the NaOH solutions was allowed to react separately with the hydrochloric acid solution and the heat effect recorded. Each set of twelve points constituted one experimental run. The electrical calibration (described in Section 3.3) was carried out before each pair of solutions was reacted. Fresh NaOH solutions were made up before each experimental run. Before each pair of solutions was reacted, it was necessary to set the baseline on the recorder by pumping through the solvent, i.e. 0.1 mol dm⁻³ NaClO₄ solution. It is not necessary to titrate each NaOH solution with the acid solution to determine the heat of neutralization since the reaction is fast and complete. The reaction between equimolar concentrations of HClO₄ and NaOH would be sufficient. However, a complete set of titration experiments was carried out as a convenient method to test the calorimetric procedure to solve any problem that may arise in future, e.g. choice of pump flow rate, recorder settings, etc.

4.3 Densities of the HClO₄ and NaOH solutions

The masses of the solutions delivered were determined by weighing the flasks before and after starting the pumps. To determine the volume and hence the number of moles of reactant delivered, the densities of each solution had to be measured at 25°C. The number of moles reacted is required in order to calculate the enthalpy change of the reaction. The densities of the titrant NaOH solutions are shown in Table 4.1. The density of the HClO₄ solution is also reported. The densities were measured using a Paar densitometer (see Section 6.6). A single set of measurements were made for each solution.

The densities of the reactant solutions were practically the same, indicating that densities of dilute solutions are largely independent of concentration.

Table 4.1

Densities at 25.00°C of titrant NaOH solutions used in the calibration of the calorimeter.

T_{air}	= 1.3361
T_{water}	= 1.8496
ρ_{air}	= 0.001138 g cm ⁻³
ρ_{water}	= 0.99704 g cm ⁻³
k	= 0.6089 g cm ⁻³

NaOH concentration/ mol dm ⁻³	T reading	Density/ g cm ⁻³
0.0050	1.8530	1.0049
0.0055	1.8530	1.0049
0.0060	1.8530	1.0048
0.0065	1.8530	1.0048
0.0070	1.8530	1.0048
0.0075	1.8530	1.0048
0.0080	1.8530	1.0048
0.0085	1.8530	1.0048
0.0090	1.8530	1.0047
0.0095	1.8530	1.0048
0.0100	1.8530	1.0047
0.0105	1.8530	1.0047

The T value for 0.0100 mol dm⁻³ HClO₄ solution was 1.8530. The corresponding density was 1.0048 g cm⁻³.

4.4 Heat of dilution of HClO₄ and NaOH

In conventional titrations, the titrant is usually diluted by a large factor while the titrate undergoes a very small dilution. In these experiments, both reactants are diluted to a similar extent in the flow cell. However, it is still necessary to determine the heats of dilution of the reactants and account for this heat as a correction in the final calculation of the heat of neutralization. Since the perchloric acid is in excess, it would immediately consume the NaOH and hence no heat of dilution for NaOH is expected.

The heat of dilution of HClO₄ was measured by pumping through 0.01 mol dm⁻³ HClO₄ and 0.1 mol dm⁻³ NaClO₄ solutions simultaneously and determining the heat effect. No deflection from the baseline was observed, indicating that the heat of dilution of 0.01 mol dm⁻³ HClO₄ is below the detection limit of the calorimeter. Thus no corrections needed to be made for the heats of dilution.

4.5 Calorimetric data for the heat of neutralization

The calorimetric data for the heat of neutralization is shown in Table 4.2. The concentrations of the NaOH titrant solutions are shown. The amount of product, viz. water, formed is determined by the limiting reagent in each pair of solutions reacted. The minimum of the molar flow rates of HClO₄ and NaOH indicates the limiting reagent. Thus the amount of water formed is determined by calculating the product of the minimum of the molar flow rates of the NaOH and HClO₄ solutions and the reaction time. The heat effect of each reaction is also shown. From this data the enthalpy change for the heat of neutralization, ΔH_N , was calculated by making use of the following equation:

Table 4.2

Calorimetric data for the aqueous heat of neutralization between the strong base, NaOH, and 0.01000 mol dm⁻³ HClO₄.

Run 1

[NaOH]/ mol dm ⁻³	Moles of H ₂ O formed/ 10 ⁻⁵ mol	Heat liberated/ J
0.0050	6.125	3.441
0.0055	6.408	3.727
0.0060	7.202	3.945
0.0065	6.662	3.768
0.0070	7.090	3.957
0.0075	8.447	4.629
0.0080	10.58	5.751
0.0085	9.494	5.105
0.0090	10.16	5.590
0.0095	10.35	5.732
0.0100	10.41	5.964
0.0105	10.37	5.934

Run 2

[NaOH]/ mol dm ⁻³	Moles of H ₂ O formed/ 10 ⁻⁵ mol	Heat liberated/ J
0.0050	4.930	2.660
0.0055	5.403	2.926
0.0060	5.905	3.174
0.0065	6.388	3.387
0.0070	6.849	3.724
0.0075	7.240	3.937
0.0080	7.605	4.237
0.0085	8.134	4.522
0.0090	8.727	4.789
0.0095	9.310	5.056
0.0100	9.704	5.392
0.0105	9.833	5.499

Run 3

[NaOH]/ mol dm ⁻³	Moles of H ₂ O formed/ 10 ⁻⁵ mol	Heat liberated/ J
0.0050	5.016	2.766
0.0055	5.485	3.015
0.0060	5.945	3.245
0.0065	6.537	3.600
0.0070	6.937	3.777
0.0075	7.299	3.989
0.0080	7.787	4.256
0.0085	8.483	4.628
0.0090	8.976	5.054
0.0095	9.528	5.284
0.0100	10.11	5.533
0.0105	10.22	5.745

$$\Delta H_N = \frac{H}{m_p} \quad (4.1)$$

where H is the heat measured (in joules) and m_p is the number of moles of product formed.

For the general reaction,



the heat of neutralization is denoted by ΔH_N . Literature values for the heat of neutralization are most often reported as the reaction enthalpy at infinite dilution, i.e. ΔH_N° .

ΔH_N° can be determined calorimetrically by determining the heat of neutralization, ΔH_N , at a particular ionic strength, μ , and correcting this to $\mu=0$ using appropriate heat of dilution data. A value obtained by this method was $-55.794 \pm 0.063 \text{ kJ mol}^{-1}$ [125].

A second method to calculate ΔH_N° is to determine ΔH_N in a series of increasingly diluted reactants with a direct linear or parabolic extrapolation of ΔH_N° , using the Debye-Hückel equation. Data treated in this way resulted in a value of $-55.815 \pm 0.04 \text{ kJ mol}^{-1}$, which is the accepted literature value at $\mu=0$ [126]. From the data shown in the tables above, an average value of $-55.156 \text{ kJ mol}^{-1}$ was obtained, which is approximately within 1.2% of the accepted value, albeit at an ionic strength of 0.1 mol dm^{-3} .

Since the experimental value for the heat of neutralization compared favourably to the literature values, it was concluded that subsequent data obtained from the calorimeter could be used with confidence.

CHAPTER FIVE

CALCULATION TECHNIQUES

In this chapter the different calculation techniques and computer programs used in this work will be described. These include a description of the corrections which have to be applied to the 'raw' calorimetric data to obtain ΔH° values. The various computer programs used to process this data will also be described.

5.1 Calculation of extraneous heat corrections for calorimetric data

The gross heat liberated in the reaction between two components in a flow-mix reaction cell consists not only of the heat of the reaction of interest but also of other side reactions and other extraneous effects, e.g. frictional heat effects. Thus the calculation of ΔH° values from titration calorimetric data requires that these extraneous heat effects are separated from the desired heats. It is first necessary to determine the source of these heat effects and then to quantify them since these differ depending on the type of instrument and procedure used. In general, however, the following steps are carried out to determine ΔH° values from calorimetric data:

- (i) the determination of the gross heat liberated in the reaction vessel as a function of titrant added,
- (ii) the calculation of all 'non-chemical' heat effects in the reaction vessel,

- (iii) the determination of heat effects contributed from other side reactions, and
- (iv) the heat solely due to the reactions of interest and then the ΔH° values.

The gross heat liberated by a reaction taking place in a flow-mix reaction cell is amplified and represented on a recorder as a plot of power versus time. A typical signal for a flow calorimetric experiment is shown in Figure 5.1.

The zero signal (A) is the voltage measured when no solution is flowing through the calorimeter. The zero value is close, but not equal, to zero. At point B, the pumping of the solvent medium is initiated. At point C, a steady state signal is attained, which serves as the baseline value for the experiment. The difference between this value and the zero value is primarily as a result of viscous flow through the calorimeter. At D, the two reactants are pumped through the reaction vessel and a steady state signal is obtained. The difference between this signal (D) and the baseline signal (C), denoted by D_{exp} , is proportional to the heat effect Q . The electrical calibration signal is identical to Figure 5.1 from which the calibration deflection, D_c , is obtained. The heat effect Q is calculated by multiplying D_{exp} by the calibration constant, ϵ (see Section 3.3).

'Non-chemical' heat effects mainly consist of heat contributed from the physical interactions of the reacting components. A major advantage of flow calorimetry is that there are very few corrections to be made compared to other batch type calorimeters where corrections for a number of effects such as heat of stirring, vapour space corrections, evaporation and condensation phenomena are required. The only non-chemical contribution to the heat measured in a heat-conduction flow calorimeter is caused by the temperature difference between the reaction vessel and the reacting solutions. This correction is accounted for by

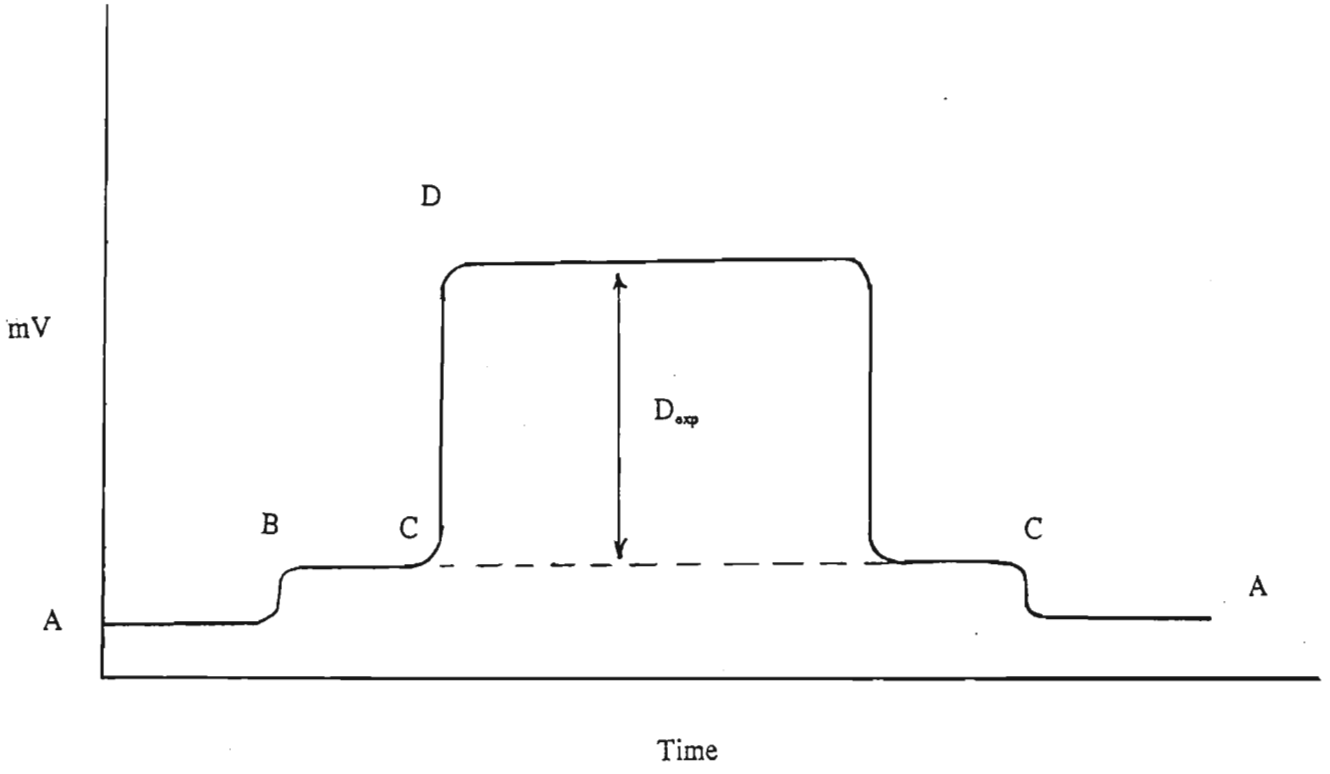


Figure 5.1 Typical signal for a flow calorimetric experiment.

pre-equilibrating the reactant solutions to the calorimeter temperature before they reach the reaction cell (see Section 3.2). The frictional heat caused by the flow of liquids in the tubing and the flow-mix cell is compensated for by incorporating this in the baseline signal (see Section 6.1.2).

If reactions other than the reaction of interest occur in the calorimeter, corrections must be made for their energy contributions to the total heat effect. These side reactions that may contribute heat to the gross heat liberated consist mainly of the heat of dilution of the reactants, heat of neutralization, protonation of the ligand and the hydrolysis of the metal ion. These heats may be determined by experimentation or from data compilations available in the literature [127].

Once the extraneous heat effects have been identified and quantified, the corrected calorimetric data and specified number of reactions is input to a computer program which apportions the overall heat effect to each of the reactions and then calculates the ΔH° values.

5.2 Use of computer programs

A number of computer programs were used to process the calorimetric data and determine the distribution of species in solution. The use of each of these programs will now be described.

5.2.1 PREKAL

The computer program PREKAL is an input program written in FORTRAN for the program

LETAGROP KALLE [38], which calculates values of ΔH° from titration calorimetric data.

The data supplied to PREKAL are converted into a format compatible with the input requirements of LETAGROP KALLE and stored in a data file accessed by LETAGROP KALLE. The data required by PREKAL consist of:

1. the concentrations of the reagents in the titrate and titrant,
2. the initial volume of the titrate,
3. the titration data in the form of total volume added up to the k-th point and (corrected) heat liberated between (k-1)th and k-th points,
4. the complexes assumed present,
5. the known or estimated values of the cumulative enthalpy changes for the above-mentioned complexes, and
6. the stability constants for the complexes assumed present.

5.2.2 LETAGROP KALLE

In this work the computer program LETAGROP KALLE [38] was used to calculate values of ΔH° from calorimetric data. LETAGROP KALLE is one of a suite of programs known as LETAGROP VRID [128] that use the "pit-mapping" minimisation technique (see Section 1.4.1) to provide the least-squares estimates of the parameters of interest.

The necessary inputs are provided via PREKAL (see Section 5.2.1). LETAGROP KALLE corrects the data for the effect of side reactions (e.g. heat of neutralization) and then produces values of ΔH° for the reactions of interest.

5.2.3 HALTAFALL

The computer program HALTAFALL is a general program for calculating the concentrations of species in an equilibrium mixture. It can treat a mixture of several components which can form a number of complexes and solid phases. The calculations can be carried out if one specifies the overall concentrations of the components, the relevant equilibrium constants (known or estimated, expressed as stability constants), and a description of the composition of the mixture.

In this study the program was used to simulate titrations in a single solution phase. In order to do this, values of the stability constants and concentrations of each set of reactants were entered. The program calculates the distribution of each postulated species as a function of pH.

A modified version of the standard HALTAFALL program, viz. HALTA1, was developed in order to calculate the ionic strength at each point of the titration. The only additional input information required is the concentration of the inert electrolyte and the charges of all the complexes present. This version of the program is useful in verifying that an approximately constant ionic medium is present during the titration.

The program HALTAFALL was also used to calculate species distributions by using the known stability constants of the species present in a particular system. This information was used to confirm which species were present in solution for the conditions under which the calorimetric titration was carried out. If each species was present in sufficient concentration then its heat of formation would contribute to the overall heat effect. This would entail taking

their heats of formation into account when calculating the ΔH° values. It was found that all metal hydrolysis products were present in extremely low concentration and hence their heats were negligible compared to the overall heat effect.

5.2.4 QUATTRO PRO

Several specialised spreadsheets were designed using this commercially available package to perform several repetitious calculations and to graphically represent data obtained as output from HALTAFALL.

5.3 Programs written by the author

Several programs were written in the computer language GWBASIC by the author of this thesis to enable one to quickly calculate the volumes required to prepare solutions of the desired composition, ionic strength and concentration, taking into account the volume contraction on mixing aqueous and organic phases. The listings of these programs are shown in the Appendices. Each program will be briefly described.

5.3.1 DIOX

This program calculates the volumes of pure dioxane and standard sodium perchlorate solution required to prepare a solution of specified composition and ionic strength.

5.3.2 DEPROT

This program calculates the volumes of standard solutions, water and pure dioxane required to give a solution of deprotonated KELEX 100. The input requirements are the concentrations of the background electrolyte, ligand and sodium hydroxide stock solutions. The program calculates a 10% excess of NaOH solution to be added to ensure that all of the ligand is deprotonated.

5.3.3 METAL

This program calculates the volumes of standard solutions, water and pure dioxane required to give a solution of a metal ion of a specified concentration. The input requirements are the concentrations of the background electrolyte and the metal ion stock solution. This program was used to prepare a series of metal ion solutions of increasing concentration to be used in the titration.

CHAPTER SIX

EXPERIMENTAL PROCEDURE

The conditions for performing the calorimetric experiments were chosen such that minimal corrections needed to be made to the overall heats measured. However, heat evolution and absorption takes place for all types of processes and systematic errors can easily be introduced into calorimetric measurements. The risk of significant systematic errors is naturally greater in microcalorimetry than when large quantities of heat are measured. There are several sources of errors, e.g. mechanical effects (friction), evaporation and condensation processes, adsorption processes, etc [129]. In practice, many errors will be accounted for by the procedure used for calibration of the method [130]. However, cognisance must be taken of other errors and the experimental procedure modified to minimise them. Generally, the practical advantages that flow calorimeters offer over other calorimeters are that there are far fewer experimental calibration procedures to be carried out to account for external heat effects. This chapter will discuss the possible sources of error that arise in microcalorimetry, how these errors were minimised in the experiments formed and a description of the experimental procedures adopted.

6.1 Errors in microcalorimetry

The errors encountered in the measurement of heats of reaction by using a flow calorimeter will now be discussed.

6.1.1 Errors in electrical calibration

Ideally, in a flow calorimeter, reactant solutions pumped in at a constant flow rate will give rise to a constant heat effect and eventually reach a steady state condition where the total heat generated (including those due to 'non-chemical' heat effects) in the cell will be equal to the heat transported from the cell by heat conduction through the surrounding thermopile. Only under these conditions will the measured heat effect be proportional to the extent of reaction in the cell. However, even at steady state, part of the heat generated is lost through the air gap between part of the flow surface not in contact with the thermopile and this heat will leave the cell with the effluent liquid [131]. The location of these heat losses in the reaction cell is shown in Figure 6.1. As described in Section 3.3, the electrical calibration constant, ϵ , is determined by electrically generating a known heat effect, P_c , in the reaction cell and measuring the recorder deflection, D_c . The value of ϵ is the quotient of these two quantities, i.e. P_c/D_c . In the absence of heat leakage between the reaction cell and the thermopiles, it is expected that the value of ϵ would be independent of any change in the flow rate of the solution used in the calibration experiment. However, Poore *et al.* [132] found that the electrical calibration constant, ϵ , varied linearly with the flow rate for a constant electrical input. For flow rates between 0 and 24 cm³ hr⁻¹, the value of ϵ differed by 6% indicating that only 94% of the heat generated in the flow cell will pass through the thermopile at such a flow rate [132]. This error in ϵ can be accounted for performing all experiments at a fixed flow rate, as was done in this work.

Electrical output is usually measured by multiplying the observed recorder deflection by ϵ . It is assumed that by performing the electrical calibration under the same experimental conditions as those of the reaction, any effects of thermal disequilibrium will contribute

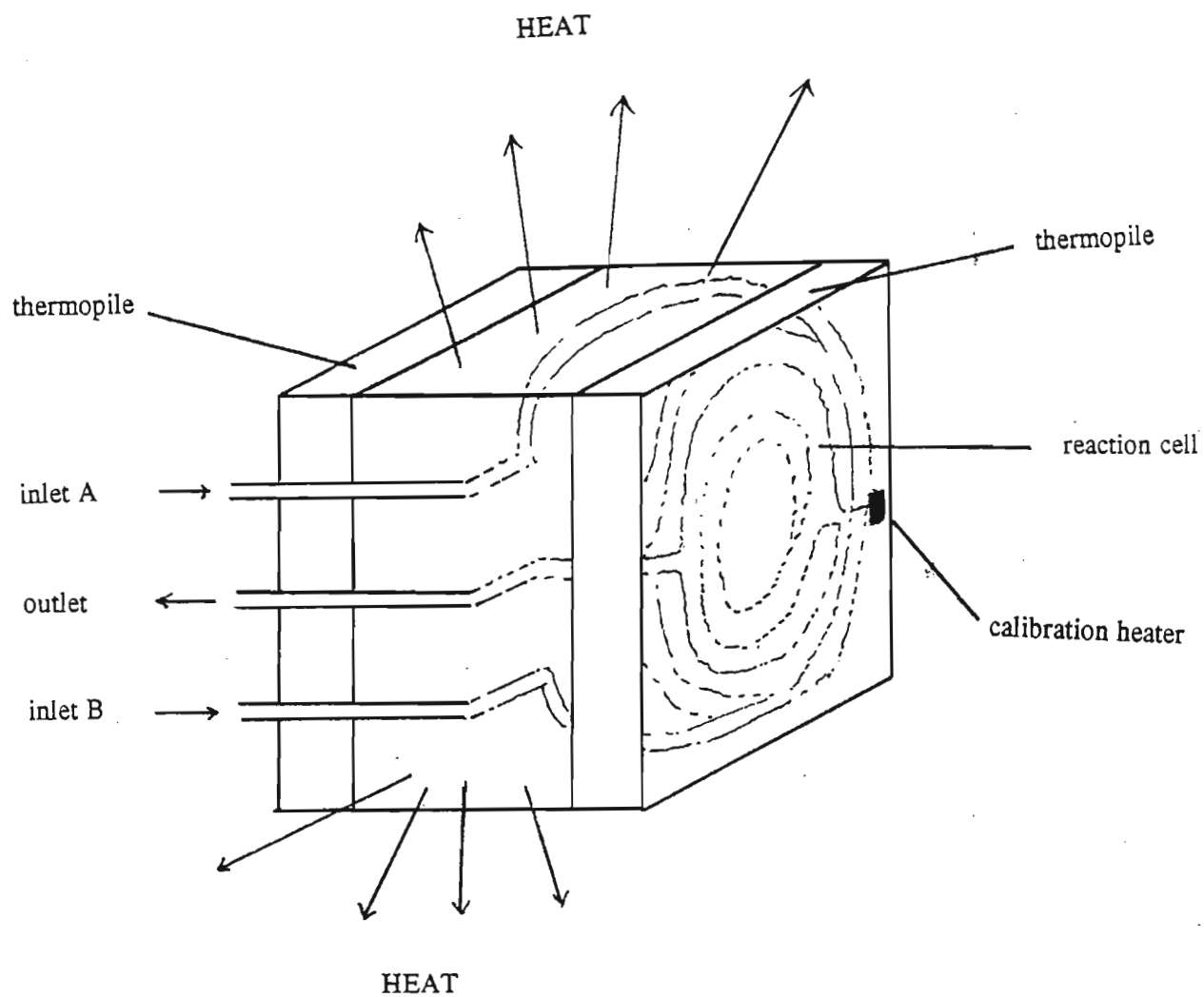


Figure 6.1 Diagram of the reaction cell, showing the location of the heat losses.

equally to the observed heat change irrespective of whether the source is chemical or electrical. This assumes that the rate of heat dissipation from the cell is constant whether heat is generated in the whole chamber or in the small calibration heater located in the base of the cell. This implies that the measured heat of reaction should exhibit a heat loss, related to liquid flow, that is identical to that observed for a constant electrical output. Poore *et al.* [132] proved this assumption false by demonstrating that the heat change for a constant electrical output was dependent on flow rate and, further, the heat change observed for a fast chemical process was directly proportional to flow rate. However, at low flow rates, the heat loss is very small and the error incurred by performing the conventional calibration (at the same flow rate as the reaction) is very small. In this work this error was minimised by performing the experiments at reasonably low flow rates.

6.1.2 Frictional effects and viscous flow

The nature of flow calorimeters is that there must be some turbulent heat associated with liquid flow and it is necessary to account for this power produced by viscous heating in the flow cell. With a heat-conduction calorimeter, this is incorporated in the "baseline value". This is established usually by pumping the solvent medium through the calorimeter. The baseline value accounts primarily for viscous heating but may, in addition, also account for other effects possibly due to insufficient temperature equilibration of the incoming flow, pressure effects on the thermopile and on the liquid flow [130]. For dilute aqueous solutions, the baseline value is often very close to the zero flow rate value but for viscous liquids, especially at high flow rates, the difference can be substantial. It is thus important that the liquid used in experiments to set the baseline has flow properties that are very similar to the reactant solutions. In this work baseline value was set by pumping in 75% (v/v) 1,4-dioxane-

water solution made up to an ionic strength of 0.1 mol dm^{-3} with NaClO_4 since it was in this medium that all calorimetric measurements were carried out.

6.1.3 Errors due to other effects

Mechanical heat effects due to agitation or stirring of the reaction solution are absent in a flow calorimeter. Evaporation and condensation are processes that evolve considerable amounts of heat (43.9 kJ mol^{-1} for ΔH_{vap} for water, i.e. 2 MJ for every 1 g H_2O evaporated) [129]. There is no gas phase present in a flow calorimeter so these sources of error are also absent. Heat effects due to adsorption or desorption of reagents from the walls of a calorimetric vessel are usually neglected in macrocalorimetry but in microcalorimetry the ratio between wall surface area and the total heat quantity measured is more unfavourable and sorption phenomena can seriously affect results. In flow microcalorimetry, no sorption effects are expected because the adsorption sites are generally saturated with the reaction mixture at the beginning of the experiment and when the instrument reaches a steady state, there are no net effects from sorption processes [129]. Specific adsorption of solute to the cell walls or tubing alters the effective concentrations of reactants only in the case of very dilute solutions, i.e. $< 10^{-9} \text{ mol dm}^{-3}$ [133]. In this work the solutions used were much more concentrated than this value and hence adsorption effects were considered to be negligible.

6.2 Outline of experimental procedure

The experimental procedure used in the experiments performed here was as follows:

A solution of constant concentration of one reactant (titrate) was used. For the titrant

solutions, a series of twelve solutions of increasing concentration at constant ionic strength of 0.1 mol dm^{-3} in 75% (v/v) 1,4-dioxane-water were prepared. The concentrations were chosen such that the mole ratio of titrant to titrate varied between 0.2:1 to 2.4:1. Each of the titrant solutions was allowed to react separately with the titrate solution. A single experimental run thus consisted of 12 flow experiments which are required to collect a complete set of data. These runs were repeated until three reproducible sets of data were obtained.

6.3 Experimental procedure

The actual procedure carried out will now be discussed in detail.

The settings on the calorimeter and thermostat units are described in Section 3.6. In all cases, the recorder speed was 5 mm min^{-1} , the recorder scale was 10 mV and the calibration current was usually set at 7.0 mA.

The assumption made in flow calorimetry is that the liquid exiting the reaction mixing vessel is in thermal and chemical equilibrium. For slow reactions, this is obviously not true. However, with fairly fast reactions like those studied in this work, the reaction time has to be such that chemical equilibrium is attained within this time. To ensure complete reaction and steady state conditions, the reaction time should exceed the residence time in the reaction cell and the connecting tubing. With heat conduction calorimeters, the response time of the instrument is of the order of minutes rather than seconds. Thus the instrument response time may be compensated for by allowing a constant flow of reactants for a length of time equal to at least 6 time constants of the calorimeter so that the data represent a thermal equilibrium

condition [134]. The time constant, τ , of the flow calorimeter used in this work was 1.5 minutes and hence 6τ is 9 minutes [135]. The residence time for the flow calorimeter was determined by noting the time taken for a steady state to be achieved (as shown by the curve on the recorder) from the time the two reactants are pumped through. This was found to be approximately 11 minutes. Further investigation of a few pairs of reactants of different concentrations (metal ion and ligand solutions) showed that a reaction time of 15 minutes was sufficient to attain steady state conditions. However, it was decided to extend this time to 30 minutes to ensure that a straight line was observed on the recorder which simplifies the measurement of the recorder deflection.

With a heat conduction calorimeter the time between the initiation of heat production from either an electrical calibration run or a chemical experiment and the establishment of a steady state condition is of the order of tens of minutes. During this period, the baseline of the instrument may drift from that measured at the beginning of the experiment. The baseline drift was shown by Hansen *et al.* [136] to be very dependent on the temperature stability of the heat sink enclosing the reaction cell and on the effect of temperature variations on the electrical signal amplification equipment. It has been shown by Mudd *et al.* [137] that in order to achieve peak-to-peak baseline noise and long-term drift of less than $0.1 \mu\text{W}$ in a heat conduction calorimeter, the air bath in which the heat sink block and reaction cell is housed must be thermostatted to within 1×10^{-4} K. The thermostat used in this work could only be controlled to about 4×10^{-3} K and it was thus necessary to reset the baseline prior to each experiment by pumping the solvent solution through the calorimeter. Also, the reactant solutions had to be flushed out before electrical calibration could be performed by pumping the solvent solution (75% (v/v) 1,4-dioxane-water solution made up to an ionic strength of 0.1 mol dm^{-3} with NaClO_4) for a time at least greater than the total residence time. A time

of 15 minutes was found to be adequate.

The experimental procedure consisted of the following steps:

- (i) the solvent solution (75% (v/v) 1,4-dioxane-water solution made up to an ionic strength of 0.1 mol dm^{-3} with NaClO_4) was pumped through both pumps for at least 15 minutes to set the baseline,
- (ii) the two reactant solutions were preweighed into the special dispensing flasks (described in Section 3.7) and then pumped through simultaneously for 30 minutes and the flasks weighed again,
- (iii) the solvent solution was again pumped through both pumps for 15 minutes to flush out the remaining reactants and to reset the baseline, and finally
- (iv) the electrical calibration was performed by switching on the calibration current for 30 minutes.

6.4 Preparation of calorimeter prior to and after use

As the calorimeter is not in use all the time it is possible for bacterial growth to take place in the reaction cell and the tubing. It was found that ethanol was effective in cleaning the cell and tubing. Every morning before use, ethanol was pumped through the reaction vessel for at least 20 minutes, followed by water for another 20 minutes. The calorimeter was now ready for use. At the end the day, warm ethanol (ca. 40°C) was flushed through the reaction cell and water pumped through again. Pumps were switched off and tubing removed. Water was allowed to stand in the mixing vessel overnight.

6.5 Densities of solutions

The peristaltic pumps deliver erratic volumes of liquid especially at low flow rates. It was therefore preferable to determine the exact mass of each solution delivered and then to calculate the exact volume delivered from the density of the solution. It was therefore necessary to measure the densities of all reactant solutions.

A Paar Precision DMA 60 Density Meter was used to measure densities.

This instrument uses a sonic wave to determine a value T (the period of oscillation), for each solution or mixture injected in the measuring cell [138]. The cell was kept at a constant temperature of $25.00 \pm 0.01^\circ\text{C}$ by circulating water from a constant temperature water bath.

Before each injection, the measuring cell (which had a volume of 0.7 cm^3) was rinsed with acetone and dried with a stream of air until a stable, reproducible reading was achieved. A volume of the solution to be tested was injected gently into the cell, taking care to avoid the introduction of air bubbles. The cell was equilibrated to 25.00°C for 5 minutes. The experimental value of T was noted. This value can be converted to the density of the test solution ρ_i , as follows:

$$\rho_i - \rho_{\text{water}} = A(T_i^2 - T_{\text{water}}^2) \quad (6.1)$$

The value of the calibration constant A was calculated from the known densities of air and water at the atmospheric pressure and temperature used, and their respective values for T [139]:

$$\rho_{air} - \rho_{water} = A(T_{air}^2 - T_{water}^2) \quad (6.2)$$

The densities of air and water were $0.0011030 \text{ g cm}^{-3}$ and $0.99710 \text{ g cm}^{-3}$ respectively [140].

Solutions were made up in 75% (v/v) 1,4-dioxane and at an ionic strength of 0.1 mol dm^{-3} . The values of T for the HClO_4 solutions of different concentrations, $0.01000 \text{ mol dm}^{-3}$ NaOH and $0.01000 \text{ mol dm}^{-3}$ deprotonated KELEX 100 in excess base (denoted by KELEX 100) were recorded. The results of these measurements, obtained in duplicate, shown in Table 6.1. The values of T for the Pb(II), Ni(II) and Cd(II) metal ion solutions are shown in Tables 6.2, 6.3 and 6.4 respectively. A single set of measurements was performed on these solutions.

6.6 Determination of the volume contraction factor on mixing aqueous solutions with 1,4-dioxane

A contraction in volume occurs when aqueous solutions are mixed with 1,4-dioxane, i.e. the volumes are not additive. The extent of contraction depends on the composition of the final mixture and must be measured in order to accurately prepare standard solutions of the correct ionic strength. This is done by measuring the volume contraction factor which is the ratio of the volume of the final mixture and the initial volumes of the component solutions.

In literature regarding work done in partially aqueous media, the solvent compositions are generally reported as a percentage (v/v) of the non-aqueous component (see, for e.g., ref [141]). The solvent composition in all cases was 75% (v/v) 1,4-dioxane and the ionic strength was maintained at 0.1 mol dm^{-3} with NaClO_4 .

Table 6.1

Densities of HClO₄ solutions made up in 75% (v/v) 1,4-dioxane at an ionic strength of 0.1 mol dm⁻³ NaClO₄.

Data set 1

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$$\text{For } 0.01000 \text{ mol dm}^{-3} \text{ NaOH: } T = 1.8701, \rho = 1.0434 \text{ g cm}^{-3}$$

$$\text{For } 0.01000 \text{ mol dm}^{-3} \text{ KELEX 100: } T = 1.8704, \rho = 1.0441 \text{ g cm}^{-3}$$

[HClO ₄]/ mol dm ⁻³	T value	Density/ g cm ⁻³
0.0020	1.8705	1.0444
0.0040	1.8705	1.0445
0.0050	1.8704	1.0442
0.0055	1.8704	1.0442
0.0060	1.8705	1.0444
0.0065	1.8703	1.0439
0.0070	1.8704	1.0442
0.0075	1.8703	1.0439
0.0080	1.8704	1.0442
0.0085	1.8703	1.0439
0.0090	1.8703	1.0440
0.0095	1.8703	1.0439
0.0100	1.8703	1.0440
0.0100	1.8703	1.0438
0.0120	1.8703	1.0440
0.0100	1.8704	1.0441
0.0160	1.8704	1.0441
0.0180	1.8703	1.0438
0.0200	1.8702	1.0437
0.0220	1.8702	1.0437

Data set 2

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$$\text{For } 0.01000 \text{ mol dm}^{-3} \text{ NaOH: } T = 1.8701, \rho = 1.0434 \text{ g cm}^{-3}$$

$$\text{For } 0.01000 \text{ mol dm}^{-3} \text{ KELEX 100: } T = 1.8704, \rho = 1.0441 \text{ g cm}^{-3}$$

[HClO ₄]/ mol dm ⁻³	T value	Density/ g cm ⁻³
0.0020	1.8705	1.0444
0.0040	1.8706	1.0445
0.0050	1.8704	1.0442
0.0055	1.8704	1.0442
0.0060	1.8705	1.0444
0.0650	1.8703	1.0439
0.0070	1.8704	1.0442
0.0075	1.8703	1.0439
0.0080	1.8704	1.0442
0.0085	1.8703	1.0439
0.0090	1.8704	1.0440
0.0095	1.8703	1.0438
0.0100	1.8703	1.0440
0.0105	1.8703	1.0438
0.0120	1.8703	1.0440
0.0140	1.8704	1.0441
0.0160	1.8704	1.0441
0.0180	1.8703	1.0438
0.0200	1.8702	1.0437
0.0220	1.8702	1.0437

Table 6.2

Densities of Pb^{2+} solutions (in excess acid) made up in 75% (v/v) 1,4-dioxane at an ionic strength of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$.

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$[\text{Pb}^{2+}] / \text{mol dm}^{-3}$	T value	Density / g cm^{-3}
0.0020	1.8706	1.0446
0.0040	1.8706	1.0451
0.0060	1.8714	1.0456
0.0080	1.8714	1.0464
0.0100	1.8716	1.0469
0.0120	1.8717	1.0472
0.0140	1.8720	1.0479
0.0160	1.8723	1.0484
0.0180	1.8725	1.0489
0.0200	1.8727	1.0493
0.0220	1.8729	1.0499
0.0240	1.8732	1.0506

Table 6.3

Densities of Ni^{2+} solutions made up in 75% (v/v) 1,4-dioxane at an ionic strength of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$.

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$[\text{Ni}^{2+}] / \text{mol dm}^{-3}$	T value	Density/ g cm^{-3}
0.0020	1.8702	1.0436
0.0040	1.8702	1.0438
0.0060	1.8703	1.0439
0.0080	1.8704	1.0441
0.0100	1.8705	1.0442
0.0120	1.8705	1.0444
0.0140	1.8683	1.0392
0.0160	1.8683	1.0393
0.0180	1.8684	1.0396
0.0200	1.8685	1.0399
0.0220	1.8686	1.0401
0.0240	1.8687	1.0403

Table 6.4

Densities of Cd^{2+} solutions made up in 75% (v/v) 1,4-dioxane at an ionic strength of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$.

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$[\text{Cd}^{2+}] / \text{mol dm}^{-3}$	T value	Density/ g cm^{-3}
0.0020	1.8694	1.0419
0.0040	1.8700	1.0432
0.0060	1.8701	1.0435
0.0080	1.8703	1.0438
0.0100	1.8701	1.0436
0.0120	1.8702	1.0437
0.0140	1.8704	1.0442
0.0160	1.8705	1.0444
0.0180	1.8707	1.0449
0.0200	1.8710	1.0455
0.0220	1.8712	1.0459
0.0240	1.8711	1.0457

The method of determination of the volume contraction factor for this work will now be described.

The total mass of a mixture of solutions, M_{mix} , is the sum of the masses of the constituent solutions. For a 2-component mixture, such as the 1,4-dioxane-water mixture,

$$M_{mix} = M_1 + M_2 \quad (6.3)$$

where M_1 and M_2 are the masses of 1,4-dioxane and water respectively.

If equation (6.3) is expressed in terms of the densities, ρ_i , and the volumes, V_i , of the individual component solutions, then:

$$M_{mix} = (\rho_1 V_1) + (\rho_2 V_2) \quad (6.4)$$

where the subscripts 1 and 2 refer to 1,4-dioxane and water respectively.

Thus, if the densities and volumes of the component solutions can be determined, then the mass of the mixture can be calculated. If the density of the mixture, ρ_{mix} , is known, then the contracted volume of the mixture, V_{mix} , can be calculated from:

$$V_{mix} = \frac{M_{mix}}{\rho_{mix}} \quad (6.5)$$

The volume contraction factor, F_{CV} is given by:

$$F_{CV} = \frac{V_{mix}}{V_1 + V_2} \quad (6.6)$$

Substituting Equations (6.4) and (6.5) gives:

$$F_{CV} = \frac{(\rho_1 V_1 + \rho_2 V_2)}{\rho_{mix}} \cdot \frac{1}{V_1 + V_2} \quad (6.7)$$

where V_1 and V_2 refer to the volumes of the 1,4-dioxane and water, respectively, which are added together to form the mixture. The volume contraction factor is used to calculate the final total volume of the reaction mixture from the volumes of the separate component solutions used to prepare the mixtures.

Contraction factors at various 1,4-dioxane compositions were determined experimentally. A series of solutions ranging from 40% to 80% (v/v) 1,4-dioxane, in increments of 5%, were prepared by mixing appropriate volumes of 1,4-dioxane, water and aqueous 1 mol dm^{-3} NaClO_4 , in various proportions. The final ionic strength of each solution was 0.1 mol dm^{-3} . Since the volumes of each solution were known (Table 6.5), only the densities of the mixtures and the individual component solutions needed to be determined.

The values of T for $1.000 \text{ mol dm}^{-3}$ NaClO_4 , pure 1,4-dioxane and the mixtures were measured. The results, obtained in triplicate, are shown in Table 6.6.

A plot representing these results is shown in Figure 6.2.

The density of pure 1,4-dioxane (1.0279 g cm^{-3}) is in very good agreement with the literature values of 1.0280 g cm^{-3} [141], 1.0279 g cm^{-3} [142] and 1.0279 g cm^{-3} [143].

Table 6.5

Volumes used to prepare aqueous 1,4-dioxane mixtures with a constant ionic strength of 0.1 mol dm⁻³. The concentration of NaClO₄ used was 1.000 mol dm⁻³. The total volumes of the solutions before mixing was 10.00 cm³.

% (v/v) dioxane	Volume of NaClO ₄ / cm ³	Volume of dioxane/ cm ³	Volume of water/ cm ³
40	1.00	4.00	5.00
45	1.00	4.50	4.50
50	1.00	5.00	4.00
55	1.00	5.50	3.50
60	1.00	6.00	3.00
65	1.00	6.50	2.50
70	1.00	7.00	2.00
75	1.00	7.50	1.50
80	1.00	8.00	1.00

Table 6.6

Results of the measurements recorded and the calculations performed in order to determine the contraction factors for aqueous 1,4-dioxane mixtures.

Data set 1

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$$\text{For pure 1,4-dioxane : } T = 1.8632, \rho = 1.0279 \text{ g cm}^{-3}$$

$$\text{For } 1.000 \text{ mol dm}^{-3} \text{ NaClO}_4: T = 1.8840, \rho = 1.0754 \text{ g cm}^{-3}$$

% (v/v) dioxane	T value	$\rho_{\text{mix}}/\text{g cm}^{-3}$	$V_{\text{mix}}/\text{cm}^3$	Contraction factor
40	1.8669	1.0362	9.816	0.9816
45	1.8677	1.0382	9.812	0.9812
50	1.8689	1.0409	9.801	0.9801
55	1.8697	1.0426	9.800	0.9800
60	1.8701	1.0435	9.806	0.9806
65	1.8705	1.0445	9.812	0.9812
70	1.8706	1.0447	9.825	0.9825
75	1.8703	1.0441	9.845	0.9845
80	1.8700	1.0434	9.866	0.9866

Data set 2

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$$\text{For pure 1,4-dioxane : } T = 1.8632, \rho = 1.0279 \text{ g cm}^{-3}$$

$$\text{For } 1.000 \text{ mol dm}^{-3} \text{ NaClO}_4: T = 1.8840, \rho = 1.0755 \text{ g cm}^{-3}$$

% (v/v) dioxane	T value	$\rho_{\text{mix}}/\text{g cm}^{-3}$	$V_{\text{mix}}/\text{cm}^3$	Contraction factor
40	1.8669	1.0363	9.815	0.9815
45	1.8679	1.0387	9.808	0.9808
50	1.8689	1.0409	9.801	0.9801
55	1.8697	1.0428	9.798	0.9798
60	1.8702	1.0439	9.803	0.9803
65	1.8705	1.0446	9.812	0.9812
70	1.8706	1.0447	9.825	0.9825
75	1.8704	1.0442	9.844	0.9844
80	1.8700	1.0434	9.867	0.9867

Data set 3

$$T_{\text{air}} = 1.3361$$

$$T_{\text{water}} = 1.8496$$

$$A = 0.6089 \text{ g cm}^{-3}$$

$$\text{For pure 1,4-dioxane : } T = 1.8632, \rho = 1.0279 \text{ g cm}^{-3}$$

$$\text{For } 1.000 \text{ mol dm}^{-3} \text{ NaClO}_4: T = 1.8840, \rho = 1.0754 \text{ g cm}^{-3}$$

% (v/v)dioxane	T value	$\rho_{\text{mix}}/\text{g cm}^{-3}$	$V_{\text{mix}}/\text{cm}^3$	Contraction factor
40	1.8669	1.0363	9.816	0.9816
45	1.8678	1.0384	9.811	0.9811
50	1.8689	1.0409	9.803	0.9803
55	1.8697	1.0427	9.800	0.9800
60	1.8702	1.0438	9.804	0.9804
65	1.8705	1.0445	9.812	0.9812
70	1.8706	1.0447	9.825	0.9825
75	1.8704	1.0443	9.844	0.9844
80	1.8700	1.0434	9.867	0.9867

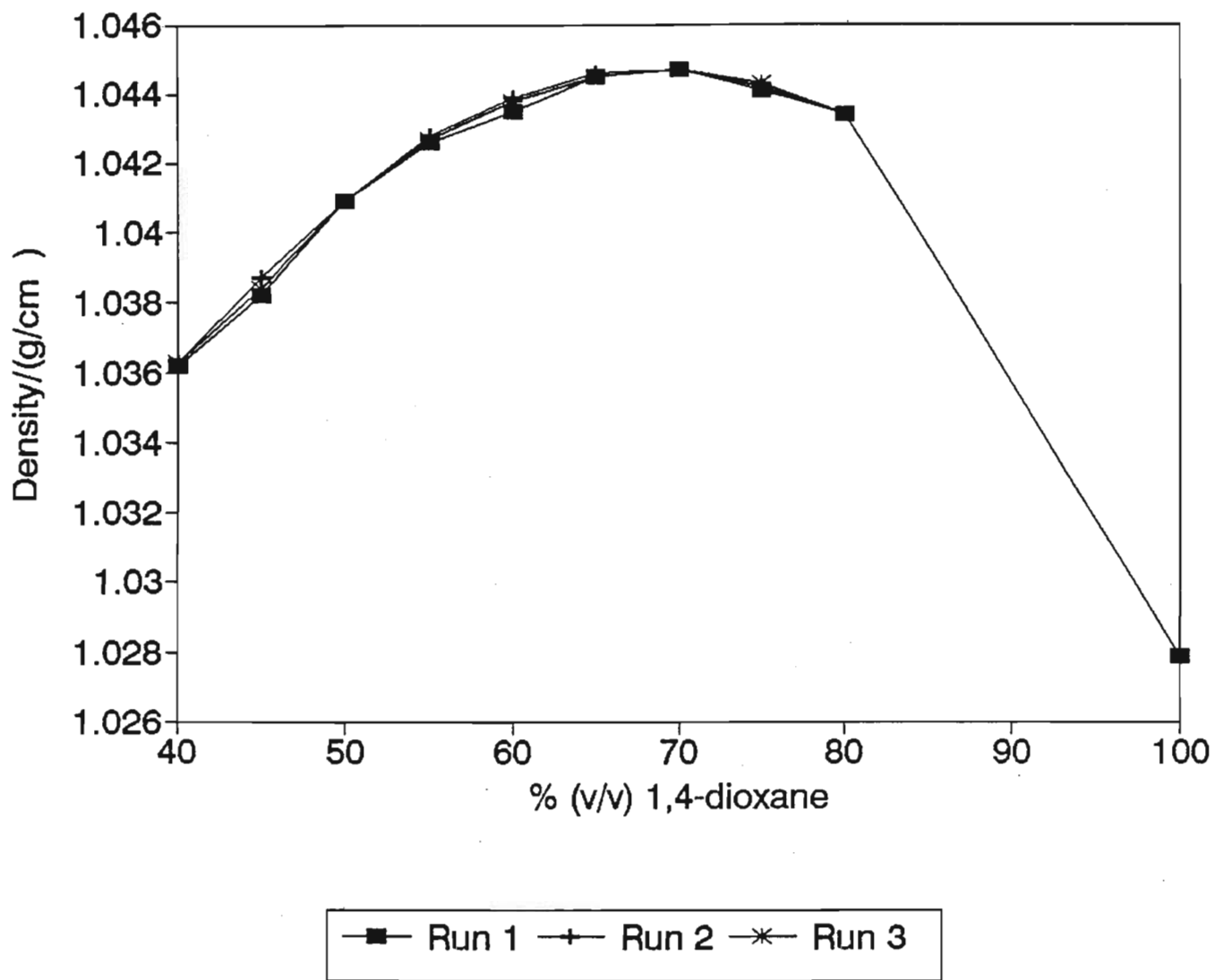


Figure 6.2 Variation in the density of aqueous - 1,4-dioxane solutions as a function of the percentage (v/v) 1,4-dioxane. All solution have an ionic strength of 0.1 mol dm^{-3}

It is difficult to compare the calculated volume contraction factors with literature values since they are not reported for the solvent composition used in this study. Irving *et al.* [67] reported a value of 0.9850 for 50% (v/v) 1,4-dioxane at 20°C and 0.3 mol dm⁻³ ionic strength. This compares to the value of 0.9802 at 25.00°C and 0.1 mol dm⁻³ NaClO₄ calculated here.

An average of the three volume contraction factors was taken for the solvent composition used in this work. Thus, for 75% (v/v) 1,4-dioxane, the volume contraction factor was calculated to be 0.9844. This value compares well with the value of 0.9838 reported by Lee [141] and is in fair agreement with the value of 0.9812 reported by Edwards [143] for a 75% (v/v) 1,4-dioxane medium under the same conditions as those used here

6.7 Determination of heat effects from chemical 'side' reactions

There are several contributions to the overall heat in the measurement of the heat of reaction between a metal ion and a ligand. The 'non-chemical' heat effects were described in Section 4.1 and these effects are largely accounted for during the electrical calibration of the calorimeter prior to use. However, there are also heats that are contributed by 'side' reactions, i.e. reactions other than the reactions of interest. The heat effects of these reactions must also be quantified and accounted for when calculating the final heats of complexation. The two main 'side' reactions in the systems studied are: (i) the heat of dissociation of water in 75% (v/v) 1,4-dioxane, and (ii) the heat of protonation of KELEX 100. The calorimetric data for these systems is shown in Table 6.7.

6.7.1 Heat of neutralization in 75% (v/v) 1,4-dioxane

The heat of neutralization in 75% (v/v) 1,4-dioxane was measured by reacting a series of HClO₄ solutions of different concentration (ranging from 0.005000 mol dm⁻³ to 0.01050 mol dm⁻³) against a standard 0.0100 mol dm⁻³ NaOH solution. This was carried out in triplicate.

6.7.2 The hydrogen ion - KELEX 100 system

The calorimetric titrations for the determination of the heats of protonation of KELEX 100 were carried out by reacting a series of increasingly more concentrated deprotonated KELEX 100 solution (concentrations varying from 0.002 mol dm⁻³ to 0.024 mol dm⁻³) with a standard 0.0100 HClO₄ solution. Each point was determined five times due to several accidents which occurred during the experimental runs, viz. the spillage of reagents and an electricity surge.

6.8 Determination of the heats of complexation of metal ions with KELEX 100

The total heat liberated by the reaction of the KELEX 100 ligand with the metal ions includes heat due to extraneous heat effects and other 'side' reactions. The total heats were measured calorimetrically and the latter heat contributions were accounted for as described in Section 5.1.

6.8.1 The lead ion - KELEX 100 system

The calorimetric titrations for the determination of the heats of reaction between the lead ion and KELEX 100 was carried out by reacting a series of increasingly more concentrated

deprotonated KELEX 100 solutions (concentrations varying from 0.002 mol dm⁻³ to 0.024 mol dm⁻³) with standard 0.0100 Pb²⁺ solution. These experimental runs were carried out in triplicate.

6.8.2 The cadmium ion - KELEX 100 system

The same procedure was carried out as for the lead ion.

6.8.3 The nickel ion - KELEX 100 system

The same procedure was carried out as for the lead ion.

6.9 Experimental data

The calorimetric data obtained for all the experiments performed is presented in Table 6.7 detailing the volumes and concentration of the reactants and the actual uncorrected heat liberated (in joules).

Table 6.7

Calorimetric data for the various systems studied.

1. **System** : $\text{H}^+ + \text{OH}^-$

Run No. 1

Titrate : $[\text{HClO}_4] = 0.0100 \text{ mol dm}^{-3}$

[NaOH]/ mol dm ⁻³	Volume of NaOH/ cm ³	Volume of HClO ₄ / cm ³	Heat liberated/ J
0.0050	8.353	8.497	2.947
0.0055	8.428	8.919	2.998
0.0060	8.410	8.877	3.269
0.0065	8.463	9.420	3.336
0.0070	8.381	9.067	3.438
0.0075	8.479	8.686	3.523
0.0080	8.370	8.822	3.844
0.0085	8.496	9.490	3.929
0.0090	8.477	9.115	3.929
0.0095	8.513	9.439	3.929
0.0100	8.726	9.452	3.963
0.0105	8.891	9.947	4.065

Run No. 2Titrate : $[\text{HClO}_4] = 0.01000 \text{ mol dm}^{-3}$

[NaOH]/ mol dm^{-3}	Volume of NaOH/ cm^3	Volume of HClO_4 / cm^3	Heat liberated/ J
0.0050	8.795	8.442	2.867
0.0055	9.611	9.741	3.106
0.0060	9.450	9.760	3.208
0.0065	9.652	8.946	3.089
0.0070	11.531	10.421	3.413
0.0075	10.103	9.482	3.208
0.0080	6.805	6.703	3.780
0.0085	7.755	7.670	3.966
0.0090	9.287	8.000	3.713
0.0095	9.980	8.230	3.781
0.0100	9.590	8.722	3.730
0.0105	9.801	9.769	3.713

Run No. 3Titrate : $[\text{HClO}_4] = 0.01000 \text{ mol dm}^{-3}$

[NaOH]/ mol dm^{-3}	Volume of NaOH/ cm^3	Volume of HClO_4 / cm^3	Heat liberated/ J
0.0050	9.182	9.514	3.108
0.0055	9.389	9.273	3.159
0.0060	9.457	9.266	3.533
0.0065	9.483	8.951	3.329
0.0070	9.887	9.873	3.940
0.0075	9.858	10.061	3.805
0.0080	9.804	9.840	4.008
0.0085	9.885	9.675	4.042
0.0090	9.616	9.489	4.246
0.0095	9.460	9.084	4.127
0.0100	9.638	9.990	4.246

2. System : H^+ + KELEX 100Run No. 1

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0110 mol dm⁻³

[HClO ₄]/ mol dm ⁻³	Volume of HClO ₄ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	8.606	7.912	0.425
0.0040	8.870	8.476	1.020
0.0060	8.724	8.500	1.734
0.0080	9.111	9.210	2.210
0.0100	9.569	9.566	2.482
0.0120	9.059	9.479	2.584
0.0140	8.365	9.794	2.737
0.0160	9.849	10.236	3.128
0.0180	8.551	9.212	3.383
0.0200	9.268	9.658	3.555
0.0220	7.331	9.783	3.555

Run No. 2

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0110 mol dm⁻³

[HClO ₄]/ mol dm ⁻³	Volume of HClO ₄ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	11.398	8.833	1.032
0.0040	9.508	8.127	1.769
0.0060	8.478	8.471	1.933
0.0080	8.229	7.763	2.376
0.0100	7.742	8.404	2.654
0.0120	7.828	8.537	2.818
0.0140	7.888	8.619	0.983
0.0160	8.291	8.920	1.655
0.0180	9.219	9.186	1.704

Run No. 3

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[HClO ₄]/ mol dm ⁻³	Volume of HClO ₄ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	8.417	7.992	1.186
0.0040	8.211	8.985	1.430
0.0060	8.453	8.645	2.145
0.0080	8.177	8.768	2.581
0.0100	8.062	8.932	2.860
0.0120	8.286	8.985	3.261
0.0140	8.438	8.116	3.715
0.0160	8.903	8.619	3.994
0.0180	8.945	9.119	4.273
0.0200	8.755	9.475	4.151

Run No. 4

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[HClO ₄]/ mol dm ⁻³	Volume of HClO ₄ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	9.634	10.531	0.542
0.0040	9.046	10.205	0.847
0.0060	7.324	10.442	1.033
0.0080	10.565	10.056	2.764
0.0100	7.839	10.013	2.560
0.0120	10.940	8.632	3.242
0.0140	8.300	9.797	3.344
0.0160	10.533	9.712	3.532
0.0180	11.104	10.795	3.788
0.0200	9.707	10.200	3.959
0.0220	9.966	10.136	4.027

Run No. 5

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[HClO ₄]/ mol dm ⁻³	Volume of HClO ₄ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	9.795	10.252	0.474
0.0040	9.347	10.425	0.881
0.0060	8.272	10.003	1.033
0.0080	7.526	9.800	2.116
0.0100	7.796	9.822	2.389
0.0120	10.627	9.523	3.225
0.0140	8.815	10.046	3.362
0.0160	10.063	9.878	3.464
0.0180	10.457	9.822	3.839
0.0200	10.064	10.567	3.925
0.0220	10.218	10.721	3.993

3. System : Pb²⁺ + KELEX 100Run No. 1

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Pb ²⁺]/ mol dm ⁻³	Volume of Pb ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated / J
0.0020	8.381	10.423	1.072
0.0040	8.860	9.809	2.490
0.0060	9.304	10.067	3.250
0.0080	7.429	9.813	3.354
0.0100	8.326	9.243	3.250
0.0120	9.241	9.468	3.458
0.0140	8.719	9.569	3.491
0.0160	9.186	9.505	3.627
0.0180	9.597	9.690	3.628
0.0200	9.204	9.297	3.388
0.0220	9.410	9.255	3.422
0.0240	9.477	9.488	3.457

Run No. 2

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Pb ²⁺]/ mol dm ⁻³	Volume of Pb ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	8.484	8.776	1.189
0.0040	8.232	9.376	2.429
0.0060	9.024	9.346	2.938
0.0080	9.345	9.572	4.008
0.0100	9.314	9.916	3.482
0.0120	9.684	9.881	3.737
0.0140	10.274	10.266	3.957
0.0160	10.622	10.457	4.076
0.0180	9.841	10.066	3.601
0.0200	9.343	9.863	3.652
0.0220	9.457	9.744	3.567
0.0240	9.293	10.003	3.567

Run No. 3

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Pb ²⁺]/ mol dm ⁻³	Volume of Pb ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	7.493	9.104	1.003
0.0040	8.993	9.739	2.265
0.0060	7.793	9.727	2.783
0.0080	9.189	9.708	3.112
0.0100	9.628	9.846	3.164
0.0120	9.364	10.111	3.458
0.0140	9.714	10.025	3.544
0.0160	10.367	10.183	3.665
0.0180	9.351	10.213	3.527
0.0200	9.488	10.264	3.682
0.0220	9.779	10.246	3.596
0.0240	10.382	10.495	3.700

4. System : Cd^{2+} + KELEX 100

Run No. 1

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Cd ²⁺]/ mol dm ⁻³	Volume of Cd ²⁺ / cm ³	Volume of KELEX 100/ cm ³	Heat liberated/ J
0.0020	9.3244	9.887	1.140
0.0040	9.604	9.371	1.930
0.0060	10.900	9.466	2.2980
0.0800	9.970	9.303	2.456
0.0100	8.929	9.711	2.736
0.0120	9.312	10.144	2.877
0.0140	11.083	10.050	2.550
0.0160	9.449	9.358	2.686
0.0180	9.559	9.351	2.720
0.0200	9.821	9.620	3.157
0.0220	9.170	9.287	3.157
0.0240	8.518	9.205	3.157

Run No. 2

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Cd ²⁺]/ mol dm ⁻³	Volume of Cd ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	7.103	7.490	1.215
0.0040	7.850	8.641	1.957
0.0060	9.206	9.411	2.328
0.0080	9.729	9.010	2.598
0.0100	8.957	9.524	2.750
0.0120	10.305	9.817	2.834
0.0140	9.212	9.019	2.598
0.0160	10.673	9.089	2.733
0.0180	10.025	9.399	2.902
0.0200	9.966	9.494	3.104
0.0220	7.366	10.206	2.936
0.0240	9.467	9.968	3.071

Run No. 3

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Cd ²⁺]/ mol dm ⁻³	Volume of Cd ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	9.161	9.588	1.252
0.0040	9.432	10.054	2.070
0.0060	9.850	9.709	2.538
0.0800	9.387	9.499	2.705
0.0100	10.164	9.597	2.805
0.0120	9.935	9.713	2.805
0.0140	10.001	9.524	2.705
0.0160	7.452	9.194	2.738
0.0180	7.610	9.362	2.705
0.0200	9.402	9.448	2.772
0.0220	9.444	9.494	3.005
0.0240	9.150	10.166	3.106

5. System : Ni²⁺ + KELEX 100

Run No. 1

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Ni ²⁺]/ mol dm ⁻³	Volume of Ni ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	7.721	8.278	1.259
0.0040	8.985	9.105	2.049
0.0060	9.307	9.482	2.754
0.0080	10.499	9.783	2.821
0.0100	8.720	9.455	2.939
0.0120	9.355	9.503	3.056
0.0140	9.705	9.745	3.459
0.0160	9.623	9.524	3.258
0.0180	9.906	9.825	3.593
0.0200	10.059	9.753	3.123
0.0220	10.800	9.486	2.922
0.0240	8.864	9.159	3.694

Run No. 2

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
[OH⁻] = 0.0010 mol dm⁻³

[Ni ²⁺]/ mol dm ⁻³	Volume of Ni ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	5.943	8.739	1.049
0.0040	8.783	7.017	2.132
0.0060	9.077	7.981	2.707
0.0080	9.132	8.419	2.538
0.0100	9.117	9.330	2.809
0.0120	9.394	9.018	3.249
0.0140	9.592	9.617	3.452
0.0160	9.359	9.052	3.519
0.0180	9.821	9.653	3.621
0.0200	9.543	9.502	3.553
0.0220	9.770	9.934	3.147
0.0240	9.523	9.832	3.215

Run No. 3

Titrate : [deprotonated KELEX 100] = 0.0100 mol dm⁻³
 [OH⁻] = 0.0010 mol dm⁻³

[Ni ²⁺]/ mol dm ⁻³	Volume of Ni ²⁺ / cm ³	Volume of (KELEX 100)/ cm ³	Heat liberated/ J
0.0020	9.052	8.993	9.137
0.0040	9.328	9.275	1.861
0.0060	9.769	9.237	2.538
0.0080	8.254	9.475	2.707
0.0100	9.653	9.526	2.707
0.0120	7.920	9.720	2.741
0.0140	9.156	9.812	3.553
0.0160	10.161	9.819	3.215
0.0180	9.251	9.719	3.350
0.0200	9.954	9.755	3.655
0.0220	9.485	9.732	3.282
0.0240	10.525	9.759	3.350

CHAPTER 7

RESULTS AND DISCUSSION

In this chapter the results derived from the calorimetric data are described and discussed in detail. The program LETAGROP KALLE was used to calculate the enthalpy changes from the calorimetric data listed in Table 6.6.

For all results listed in this work, the standard deviation calculated by the program is shown in parentheses after the appropriate result. In the calculation of enthalpy changes, the values of the stability constants were taken from the literature. Table 7.1 lists those values.

7.1 Naming convention of thermodynamic quantities

The complexation reaction between a metal ion and ligand is usually represented by the following reaction:



In aqueous and partially aqueous systems, hydrolysis of the metal ion usually occurs to some extent. Thus an additional species besides the metal ion and ligand, i.e., the hydrogen ion, H^+ , needs to be considered. Reaction (7.1) can now be written as:



Table 7.1

Stability constants used for the calculation of enthalpy changes. All data are for 25 °C, $\mu = 0.1 \text{ mol dm}^{-3}$ and 75% (v/v) dioxane. (L = KELEX 100.)

Reaction	log β	Reference
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	16.45	142
$\text{H}^+ + \text{L}^- \rightleftharpoons \text{HL}$	13.16	143
$2\text{H}^+ + \text{L}^- \rightleftharpoons \text{H}_2\text{L}^+$	15.88	143
$\text{Pb}^{2+} + \text{L}^- \rightleftharpoons \text{PbL}^+$	11.65	143
$\text{Pb}^{2+} + 2\text{L}^- \rightleftharpoons \text{PbL}_2$	20.53	143
$\text{Cd}^{2+} + \text{L}^- \rightleftharpoons \text{CdL}^+$	10.87	144
$\text{Cd}^{2+} + 2\text{L}^- \rightleftharpoons \text{CdL}_2$	19.19	144
$\text{Cd}^{2+} + 2\text{L}^- + \text{OH}^- \rightleftharpoons \text{CdL}_2(\text{OH})^-$	11.77	144
$\text{Ni}^{2+} + \text{L}^- \rightleftharpoons \text{NiL}^+$	9.92	144
$\text{Ni}^{2+} + 2\text{L}^- \rightleftharpoons \text{NiL}_2$	19.81	144
$\text{Ni}^{2+} + 3\text{L}^- \rightleftharpoons \text{NiL}_3^-$	24.34	144

In this chapter, the stepwise and cumulative thermodynamic quantities associated with the formation of a particular complex between the metal ion, M^{2+} , the ligand, L^- , and the hydrogen ion, H^+ , are defined in Table 7.2. Obviously, both the stepwise and cumulative values for the first step of a complexation reaction will be the same since they both refer to the same reaction.

7.2 Heat of neutralization in 75% (v/v) 1,4-dioxane

Few values are available in the literature for the heat of neutralization under the conditions used in this work, viz. at 25.00°C, in 75% (v/v) dioxane and at an ionic strength of 0.1 mol dm^{-3} . In some instances, the ionic strength at which the heats of neutralization were determined was not reported [145]. Table 7.3 lists the relevant values at different compositions of 1,4-dioxane and water. Aksnes [145] obtained a value of the neutralization enthalpy in 75% (v/v) dioxane but the ionic strength was not specified. This figure, however, is much lower than that obtained by Kido *et al.* [146] who investigated the activity of water in dioxane mixtures and concluded that the activity of water in a 75% (v/v) dioxane solution differs by only 10% from that of pure water. This suggested that the state of hydration of ions in this solvent may not be very different from that of water and hence the enthalpies of neutralization should be comparable. They measured the heats of neutralization in dioxane mixtures of different compositions and found a variation of only 2.4%. However, their value for the heat of neutralization in pure water ($-56.777 \text{ kJ mol}^{-1}$) is higher than the accepted value of $-55.815 \text{ kJ mol}^{-1}$ [126]. This suggests that the value of $-58.12 \text{ kJ mol}^{-1}$ in 75% (v/v) dioxane may be higher than the correct value. An average value of $-53.110 \text{ kJ mol}^{-1}$ was obtained in this work which is quite different from Kido *et al.* [146] but within 0.25% of the value given by Aksnes [145]. The heat of neutralization is the association of the proton and

Table 7.2

Naming convention of thermodynamic quantities, ΔX_{pqr} , for the formation of different complexes. X represents the thermodynamic quantity (i.e. X = G, H or S), p is the number of protons, q is the number of metal ions and r is the number of ligands in a particular complex. The presence of a hydroxide ion, OH⁻, is denoted by a negative p value.

Type	Reaction	Symbol
Stepwise	$H^+ + L^- \rightleftharpoons HL$	ΔX_1
	$H^+ + HL \rightleftharpoons H_2L^+$	ΔX_2
	$M^{2+} + L^- \rightleftharpoons ML^+$	ΔX_1
	$ML^+ + L^- \rightleftharpoons ML_2$	ΔX_2
	$ML_2 + L^- \rightleftharpoons ML_3^-$	ΔX_3
	$ML_2 + OH^- \rightleftharpoons ML_2(OH)^-$	ΔX_4
Cumulative	$H^+ + L^- \rightleftharpoons HL$	ΔX_{101}
	$2H^+ + L^- \rightleftharpoons H_2L^+$	ΔX_{201}
	$M^{2+} + L^- \rightleftharpoons ML^+$	ΔX_{011}
	$M^{2+} + 2L^- \rightleftharpoons ML_2$	ΔX_{012}
	$OH^- + M^{2+} + 2L^- \rightleftharpoons ML_2(OH)^-$	$\Delta X_{.112}$
	$M^{2+} + 3L^- \rightleftharpoons ML_3^-$	ΔX_{013}

Table 7.3

Heats of neutralization of strong acid and strong base at 25.00°C at different compositions of 1,4-dioxane and water.

Percent dioxane (v/v)	$-\Delta H / \text{kJ mol}^{-1}$	Ionic strength/ mol dm^{-3}	Reference
75	53.110 (1.465)	0.1	This work
75	52.978	Not specified	145
0	56.78 (0.08)	0.1	146
25	57.11 (0.59)	0.1	146
50	57.32 (0.17)	0.1	146
75	58.12 (0.17)	0.1	146

the hydroxide ions to form water and is also referred to as the heat of association of water. The additive inverse of this value would therefore give the heat of dissociation of water and it is this value (53.110 kJ mol⁻¹) that was used in all subsequent calculations to correct the heats measured for any heat contribution due to the dissociation of water. Since the heat of neutralization measured in this work is reasonably close to literature values, the experimental technique was considered to yield fairly reliable values for heats of reaction.

7.3. The hydrogen ion - KELEX 100 system

The protonation constants of KELEX 100, the stability constant for the dissociation of water and the enthalpy change associated with the dissociation of water in 75% (v/v) dioxane were used as inputs in the calculation of the heats of protonation of KELEX 100. The heats of protonation of KELEX 100 have not been measured before so no direct comparison could be made. The stepwise and cumulative thermodynamic quantities for the protonation of KELEX 100 are compared to those of some structurally related ligands in Tables 7.4 and 7.5 respectively. The structures of these ligands are shown in Figure 7.1.

All the protonation reactions are exothermic. For the stepwise reactions, $|\Delta H_2|$ is only slightly larger than $|\Delta H_1|$ for the alkyl substituted 8-hydroxyquinolines but not for 8-hydroxyquinoline itself and the sulphonic acid. The increased exothermicity of the second protonation may be because the electron withdrawing effect of the phenolic oxygen is neutralized by the first protonation thus enhancing the covalent nature of the N-H bond.

The stepwise enthalpies of protonation of KELEX 100 are similar in magnitude to those for the 8-hydroxyquinoline derivatives.

Table 7.4

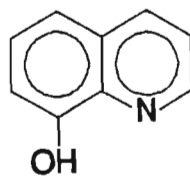
Stepwise thermodynamic parameters (in kJ mol^{-1}) for the protonation of KELEX 100 and structurally related ligands. All data is at 25.00°C and 0.1 mol dm^{-3} ionic strength. (8HQ = 8-hydroxyquinoline).

Ligand	% dioxane (v/v)	$\Delta G_1/$	$\Delta G_2/$	$\Delta H_1/$	$\Delta H_2/$	$T\Delta S_1/$	$T\Delta S_2/$	Reference
KELEX 100	75	-75.08	-15.52	-24.90 (1.13)	-27.43 (2.73)	50.72	-13.92	This work
8-HQ	50	-62.47	-23.56	-26.82	-24.39	35.64	-0.83	147
2-methyl-8HQ	50	-64.53	-26.93	-28.95	-29.12	35.58	-2.21	147
4-methyl-8HQ	50	-63.33	-27.56	-25.86	-28.20	37.46	-0.66	147
5-sulphonic-8HQ	50	-56.23	-20.33	-20.71	-16.90	35.52	3.43	147

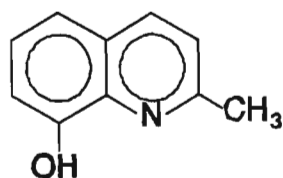
Table 7.5

Cumulative thermodynamic parameters (in kJ mol^{-1}) for the protonation of KELEX 100 and related ligands. All data is at 25.00°C and 0.1 mol dm^{-3} ionic strength. (8HQ = 8-hydroxyquinoline).

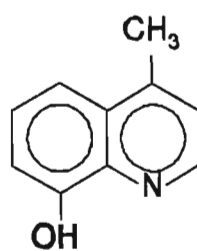
Ligand	% dioxane (v/v)	$\Delta G_{101}/$	$\Delta G_{201}/$	$\Delta H_{101}/$	$\Delta H_{201}/$	$T\Delta S_{101}/$	$T\Delta S_{201}/$	Reference
KELEX 100	75	-75.07	-90.60	-24.90 (1.13)	-52.33 (2.95)	50.17	36.80	This work
8-HQ	50	-62.47	-86.03	-26.82	-51.21	35.65	34.81	147
2-methyl-8HQ	50	-64.53	-91.46	-28.95	-58.07	35.58	33.37	147
4-methyl-8HQ	50	-63.33	-90.89	-25.86	-54.06	37.47	36.80	147
5-sulphonic-8HQ	50	-56.23	-76.56	-20.71	-37.61	35.52	38.95	147



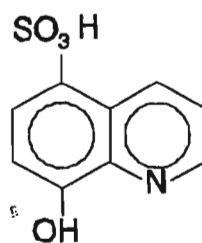
8-hydroxyquinoline



2-methyl-8-hydroxyquinoline



4-methyl-8-hydroxyquinoline



5-sulphonic-8-hydroxyquinoline

Figure 7.1 Structure of 8-hydroxyquinoline and related ligands

The first step of the protonation for all the ligands listed is accompanied by a large positive entropy change ($T\Delta S_1$) but the subsequent change in entropy ($T\Delta S_2$) is negative for the ligands except for the sulphonic acid. This has also been found for bidentate diamines [148]. The first stage of protonation involves the neutralization of the anionic ligand with the proton. The large positive entropy change for the first protonation is in keeping with Kumar's observation that a high reaction entropy indicates a combination of positive and negative ions [149]. The second stage of protonation, however, is accompanied by a decrease in entropy. This loss of entropy may be due to the reaction of the neutral, undissociated ligand which is probably poorly solvated since the ligand is uncharged in solution. Hence there is little liberation of solvent molecules which would increase the entropy. The presence of the bulky alkyl group on the KELEX 100 ligand probably limits the degree of solvation even further, which may account for its unusually large negative entropy change. For the substituted 8-hydroxyquinolines, the entropies of neutralization of the tertiary nitrogens and the phenolic oxygens are fairly constant (within experimental error), indicating that the basicity changes in the compounds are affected by enthalpies (and hence bond strengths) only.

It is seen from Table 7.5 that the cumulative heats of protonation of KELEX 100 are similar to those of 8-hydroxyquinoline but more exothermic than that of the sulphonic acid substituted complex and less exothermic than the methyl-substituted 8-hydroxyquinolines. Thus the heats of protonation of the substituted ligands would seem to depend on the type and position of the substituent.

The stability of KELEX 100 is similar to that of the substituted 8-hydroxyquinolines and the trend in Gibbs free energy is paralleled clearly by the enthalpy of the reaction rather than the entropy. Figure 7.2 shows the cumulative thermodynamic parameters associated with the

formation of the H_2L^+ complex. It is seen that the decrease in Gibbs free energy is paralleled by the increase in exothermicity of the reaction. Thus the entropy does not contribute very significantly to the stability of the protonated complexes.

The effect of increasing organic content of the solvent on the thermodynamics of ligand protonation was investigated by Steger [150] who found that the increase in stability of the protonated complexes (H_2L^+) of 8-hydroxyquinoline-5-sulphonic-acid with increasing 1,4-dioxane content could be attributed to enthalpy rather than entropy changes. He observed that the increase in average heats of reaction (i.e. ΔH_{201}) with 1,4-dioxane content was similar to the average stabilities of the complexes, as characterized by the decrease in Gibbs free energies (ΔG_{201}). The increased enthalpy change relative to the Gibbs free energy for KELEX 100 is very similar to that for 8-hydroxyquinoline-5-sulphonic-acid. The entropy change for KELEX 100 is actually lower than the value for the sulphonic acid in 50% 1,4-dioxane, emphasising that it is the enthalpy that is the dominating factor contributing to complex stability.

Generally, the stability of ligands containing an O-H bond increases with increasing organic content of the solvent [67]. The Walden-Stokes product of the limiting conductivity and viscosity in 'water-rich' solvents remains essentially constant in solutions ranging from 0 to 75% (v/v) 1,4-dioxane which indicates that the effective radii of the solvated ions remain approximately constant in this solvent range [151]. Thus the increase in the attractive forces between ions in solvents with increasing organic content is not due to changes in the sizes of the ions but rather to the decrease in the dielectric constant of the solvent. This may be due to the decrease in solvation of the ions in organic rich solvents.

It can be shown that the decrease in the dielectric constant of the medium with an increase in organic content of the solvent is the reason why the increased stability of the O-H bond for the 8-hydroxyquinoline ligand is an enthalpy rather than an entropy effect.

Enthalpy, H, and entropy, S, may be related to the dielectric constant, D, of a solution by the Kelvin-Helmholtz relations [152]:

$$H = \frac{N_i e_i^2}{2Dr_i} (1 - LT) \quad (7.3)$$

and

$$S = \frac{N_i e_i^2 L}{2Dr_i} \quad (7.4)$$

where L is an empirical constant related to the temperature and the dielectric constant by:

$$\frac{d \ln D}{dT} = -L \quad (7.5)$$

The variables N_i , e_i and r_i are the number of ions, the charge on the ions and the distance of closest approach for a spherical ion, respectively.

From equations (7.3) and (7.4) it must be shown that $(1 - LT) > -L$ to show that the enthalpy effect is larger than the entropy effect i.e. $L < 1/297 \text{ K}^{-1}$ at $T = 298 \text{ K}$ (the temperature at which these studies were carried out). Using data for the dielectric constant for 60% and 80% by mass 1,4-dioxane-water solutions [153], it can be shown that the values of L are $1.081 \times 10^{-3} \text{ K}^{-1}$ and $9.772 \times 10^{-4} \text{ K}^{-1}$ respectively. These values of L are approximately 3 and 3.5 times less than $1/297 \text{ K}^{-1}$ at 298 K respectively. Thus the enthalpy effect is shown to be the dominant factor in the increase in stability of 8-hydroxyquinoline with increasing 1,4-

dioxane content. On this basis it is expected that the enthalpy would be primarily responsible for the increase in stability of the complexes as the solvent composition increased from 50% to 75% (v/v) 1,4-dioxane.

7.4 The lead ion - KELEX 100 system

To calculate the heats of formation of the Pb-KELEX 100 complexes, the inputs for LETAGROP KALLE were the stability constants and enthalpy changes for H_2O , HL, H_2L^+ and the stability constants for ML^+ and ML_2 . No data was available in the literature to account for the enthalpies of formation of the hydrolysis products of the Pb^{2+} ion under the conditions of this work. However, using the program HALTAFALL, it was shown that there were no hydrolysis products present in any significant concentration under the conditions of the calorimetric titration. The stepwise thermodynamic parameters obtained for the formation of the $\text{Pb}(\text{KELEX 100})^+$ and $\text{Pb}(\text{KELEX 100})_2$ complexes are shown in Table 7.6 together with other literature values. The cumulative thermodynamic parameters are listed in Table 7.7. This system has not been studied before and hence no direct comparisons could be made.

The stepwise enthalpies of complexation for all ligands listed are negative indicating a favourable exothermic reaction. $|\Delta H_2| > |\Delta H_1|$ for all complexes. This successive increase in enthalpies is also observed for the reaction of metal ions with polyamines [81]. This behaviour is apparently characteristic for the reaction of 3d metal ions with polyamines and has been explained by considering that the charge on the metal ion is partially neutralized upon the addition of the first ligand molecule and hence the 'soft' character of the metal ion is enhanced, and thus its tendency to bond covalently. The reaction with a second ligand molecule will involve a more covalent interaction with a more exothermic heat of reaction.

Table 7.6

Stepwise thermodynamic parameters of complex formation for Pb(II) with KELEX 100 and related ligands. All data is at 25.00°C and 0.1 mol dm⁻³ ionic strength.

Ligand	Percent dioxane (v/v)	$\Delta G_1/$ kJ mol ⁻¹	$\Delta G_2/$ kJ mol ⁻¹	$\Delta H_1/$ kJ mol ⁻¹	$\Delta H_2/$ kJ mol ⁻¹	$T\Delta S_1/$ kJ mol ⁻¹	$T\Delta S_2/$ kJ mol ⁻¹	Reference
KELEX 100	75	-66.47	-50.66	-26.68 (0.70)	-49.02 (3.11)	39.78	1.64	This work
8-hydroxyquinoline	50	-57.22	-41.70	-27.61	-35.56	29.62	6.14	147
2-methyl-8-hydroxyquinoline	50	-56.88	-41.13	-26.36	-30.96	30.52	10.16	147
4-methyl-8-hydroxyquinoline	50	-59.68	-46.15	-28.45	-35.98	31.23	10.16	147

Table 7.7

Cumulative thermodynamic parameters of complex formation for Pb(II) with KELEX 100 and related ligands. All data is at 25.00°C and 0.1 mol dm⁻³ ionic strength.

Ligand	Percent dioxane (v/v)	$\Delta G_{011}/$ kJ mol ⁻¹	$\Delta G_{012}/$ kJ mol ⁻¹	$\Delta H_{011}/$ kJ mol ⁻¹	$\Delta H_{012}/$ kJ mol ⁻¹	$T\Delta S_{011}/$ kJ mol ⁻¹	$T\Delta S_{012}/$ kJ mol ⁻¹	Reference
KELEX 100	75	-66.47	-117.13	-26.68 (0.70)	-75.71 (3.19)	39.78	41.42	This work
8-hydroxyquinoline	50	-57.22	-98.92	-27.61	-63.17	29.62	35.76	147
2-methyl-8-hydroxyquinoline	50	-56.88	-98.01	-26.36	-57.32	30.52	40.68	147
4-methyl-8-hydroxyquinoline	50	-59.68	-105.83	-28.45	-64.43	31.23	41.39	147

The magnitude of ΔH_1 for KELEX 100 is comparable to those of the substituted 8-hydroxyquinolines, which are all similar, but the value for ΔH_2 for KELEX 100 is much higher than for the other ligands.

The stepwise entropy changes are all positive with a decrease in magnitude for the second step of chelation. This decrease may be a consequence of the partial neutralization of the charge on the metal ion which would decrease the degree of solvation. Hence less solvent molecules would be displaced leading to a lower positive entropy change. The value of $T\Delta S_1$ for KELEX 100 is highest but the value for $T\Delta S_2$ is lowest for KELEX 100. The 7-alkyl substituent on the KELEX 100 molecule makes it bulkier than the substituted 8-hydroxyquinolines and on complexation the movement of the alkyl substituent is restricted. The complexation of the first KELEX 100 molecule with the Pb(II) ion results in the loss of solvent molecules from the solvation sphere and hence an increase in entropy. The addition of the second KELEX 100 molecule would, on account of the relatively larger size of the PbL^+ complex, displace fewer solvent molecules and thus a smaller change in entropy is expected in comparison to the substituted 8-hydroxyquinolines.

It is observed from Table 7.7 that the cumulative change in Gibbs free energy for the substituted 8-hydroxyquinolines are all similar. This is due to the both the enthalpy and the entropy changes being approximately constant. This is shown in Figure 7.3 where the cumulative thermodynamic parameters for the formation of the PbL_2 complex are shown. The increase in stability of the $Pb(KELEX\ 100)_2$ compared to the other substituted 8-hydroxyquinolines is attributed to a more favourable (i.e. more exothermic) enthalpy change rather than a smaller favourable entropy change.

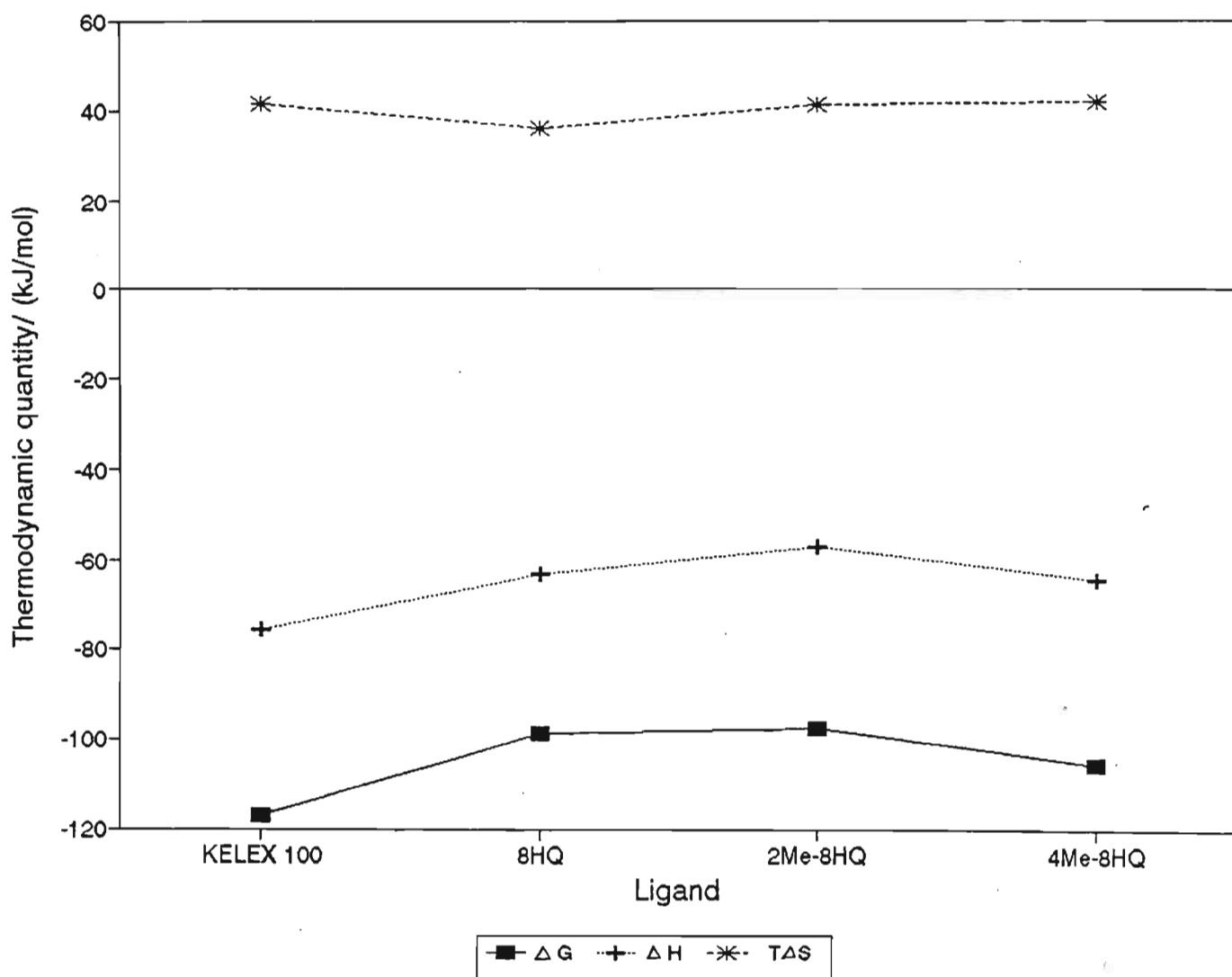


Figure 7.3

Cumulative thermodynamic parameters for the formation of the PbL_2 complexes of KELEX 100 and related ligands at 25.00°C and an ionic strength of 0.1 mol dm⁻³. All values obtained at 50% (v/v) 1,4-dioxane except for KELEX 100 which was at 75% (v/v) 1,4-dioxane. (8HQ = 8-hydroxyquinoline, 2-Me-8HQ = 2-methyl-8-hydroxyquinoline and 4-Me-8HQ = 4-methyl-8-hydroxyquinoline.)

The thermodynamic parameters measured in this work were measured at 75% (v/v) 1,4-dioxane and are not strictly comparable to those of the substituted 8-hydroxyquinolines which were determined at 50% (v/v) 1,4-dioxane. In general, it is observed that the thermodynamic quantities increase in magnitude as the 1,4-dioxane content increases. This agrees with Steger's observation [150] that the cumulative thermodynamic parameters increase with increasing 1,4-dioxane content for the complexation of 5-sulphonic-8-hydroxyquinoline with Ni(II), Mn(II), Mg(II) and Zn(II) metal ions. It is thus expected that the thermodynamic parameters for the alkyl-substituted hydroxyquinolines would be closer to the values for KELEX 100 if they were measured in 75% (v/v) 1,4-dioxane.

7.5 The cadmium ion - KELEX 100 system

To calculate the heats of formation of the Cd-KELEX 100 complexes, the inputs for LETAGROP KALLE were the stability constants and enthalpy changes for H_2O , HL, H_2L^+ and the stability constants for ML^+ , ML_2 and $\text{ML}_2(\text{OH})^-$. No data was available in the literature to account for the enthalpies of formation of the hydrolysis products of the Cd^{2+} ion under the conditions of this work. However, using the program HALTAFALL, it was shown that no hydrolysis products, except for $\text{ML}_2(\text{OH})^-$, were present in any significant concentration under the conditions of the calorimetric titration. The stepwise thermodynamic parameters obtained for the formation of the $\text{Cd}(\text{KELEX 100})^+$, $\text{Cd}(\text{KELEX 100})_2$ and $\text{Cd}(\text{KELEX})_2(\text{OH})^-$ complexes are shown in Table 7.8 together with the literature values for 8-hydroxyquinoline since thermodynamic data of chelation with Cd(II) is available only for 8-hydroxyquinoline and none of its substituted counterparts. The cumulative thermodynamic parameters are listed in Table 7.9.

Table 7.8

Stepwise thermodynamic parameters of complex formation for Cd(II) with KELEX 100 and 8-hydroxyquinoline ligands. All data is at 25.00°C and 0.1 mol dm⁻³ ionic strength.

Ligand	Percent dioxane (v/v)	$\Delta G_1/$ kJ mol ⁻¹	$\Delta G_2/$ kJ mol ⁻¹	$\Delta G_4/$ kJ mol ⁻¹	$\Delta H_1/$ kJ mol ⁻¹	$\Delta H_2/$ kJ mol ⁻¹	$\Delta H_4/$ kJ mol ⁻¹	T $\Delta S_1/$ kJ mol ⁻¹	T $\Delta S_2/$ kJ mol ⁻¹	T $\Delta S_4/$ kJ mol ⁻¹	Reference
KELEX 100	75	-62.02	-47.47	42.33	-26.56 (1.19)	-34.68 (5.66)	-45.97 (10.8)	35.46	12.78	-88.30	This work
8-hydroxyquinoline	50	-46.90	-39.94	---	-23.01	-25.52	---	23.87	14.42	---	147

Table 7.9

Cumulative thermodynamic parameters of complex formation for Cd(II) with KELEX 100 and 8-hydroxyquinoline. All data is at 25.00°C and 0.1 mol dm⁻³ ionic strength.

Ligand	Percent dioxane (v/v)	$\Delta G_{011}/$ kJ mol ⁻¹	$\Delta G_{012}/$ kJ mol ⁻¹	$\Delta G_{.112}/$ kJ mol ⁻¹	$\Delta H_{011}/$ kJ mol ⁻¹	$\Delta H_{012}/$ kJ mol ⁻¹	$\Delta H_{.112}/$ kJ mol ⁻¹	T $\Delta S_{011}/$ kJ mol ⁻¹	T $\Delta S_{012}/$ kJ mol ⁻¹	T $\Delta S_{.112}/$ kJ mol ⁻¹	Reference
KELEX 100	75	-62.02	-109.49	-67.16	-26.56 (1.19)	-61.25 (5.78)	-107.22 (12.3)	35.46	48.25	-40.06	This work
8-hydroxyquinoline	50	-46.90	-86.84	---	-23.01	-48.53	---	23.87	38.29	---	147

All of the complexation reactions were exothermic. The stepwise enthalpies of formation for KELEX 100 are more exothermic than for 8-hydroxyquinoline. The increase in exothermicity upon addition of the second ligand molecule is the same as that observed for the reaction of the Pb(II) with KELEX 100. The value of ΔH_4 for the formation of the hydroxo complex is also negative, indicating a favourable enthalpy of reaction. However, this is offset by the very large negative entropy change.

The stepwise entropies of formation are positive except for $T\Delta S_4$ for KELEX 100 which is a large negative value. $T\Delta S_2 < T\Delta S_1$ for both ligands with $T\Delta S_1$ being larger for KELEX 100 than 8-hydroxyquinoline and vice versa for $T\Delta S_2$. This type of behaviour was also observed for the complexation of the Pb(II) ion with KELEX 100. This was thought to be due to steric effects, as explained in Section 7.4.

The increase in stability of the $\text{Cd}(\text{KELEX 100})_2$ complex compared to that of 8-hydroxyquinoline is due both to favourable enthalpy and entropy changes. This is shown in Figure 7.4, where the cumulative thermodynamic parameters for the formation of the CdL_2 are plotted.

7.6 The nickel ion - KELEX 100 system

To calculate the heats of formation of the Ni-KELEX 100 complexes, the inputs for LETAGROP KALLE were the stability constants and enthalpy changes for H_2O , HL, H_2L^+ and the stability constants for ML^+ , ML_2 and ML_3^- . No data was available in the literature to account for the enthalpies of formation of the hydrolysis products of the Ni^{2+} ion under the conditions of this work. However, using the program HALTAFALL, it was shown that there

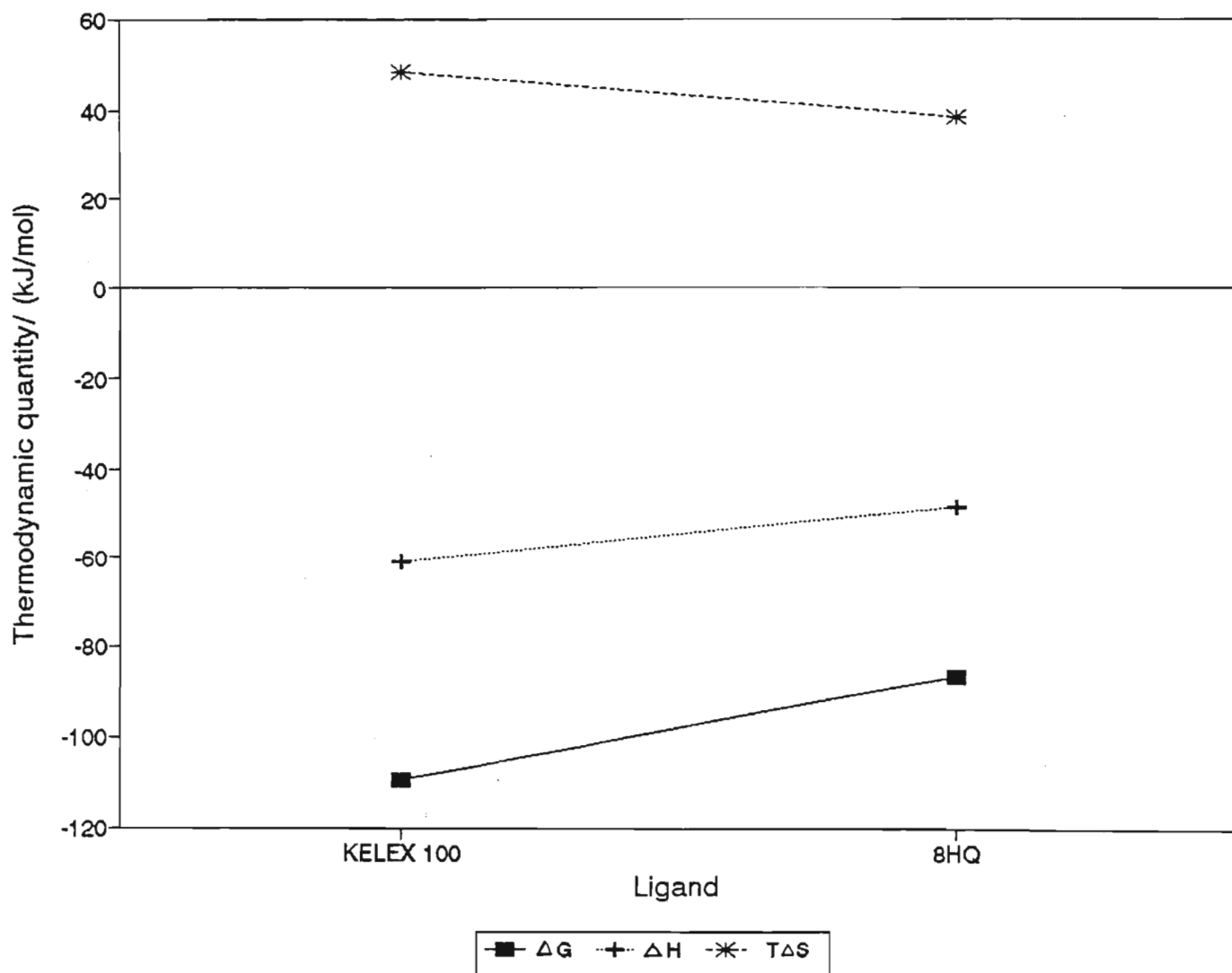


Figure 7.4 Cumulative thermodynamic parameters for the formation of the CdL_2 complexes of KELEX 100 and 8-hydroxyquinoline at 25.00°C and an ionic strength of 0.1 mol dm^{-3} . All values obtained at 50% (v/v) 1,4-dioxane except for KELEX 100 which was at 75% (v/v) 1,4-dioxane. (8HQ = 8-hydroxyquinoline.)

were no hydrolysis products present in any significant concentration under the conditions of the calorimetric titration. The stepwise thermodynamic parameters obtained for the formation of the $\text{Ni}(\text{KELEX } 100)^+$, $\text{Ni}(\text{KELEX } 100)_2$ and $\text{Ni}(\text{KELEX } 100)_3^-$ complexes are shown in Table 7.10 together with other pertinent values from the literature. Table 7.11 lists the cumulative thermodynamic parameters for the complexation reactions.

The stepwise heats of reaction are all negative with $|\Delta H_2| > |\Delta H_1|$ for all complexes except 4-methyl-8-hydroxyquinoline which shows a slight decrease. The increase in exothermicity is the same as that observed for the reactions of the Cd(II) and Pb(II) ions with KELEX 100.

The stepwise entropies of formation are positive except for $T\Delta S_3$ for KELEX 100 which is a fairly large negative value. The unfavourable entropy change for the formation of the NiL_3^- complex may be explained as follows:

The complexation of two large KELEX 100 molecules with the relatively small Ni(II) ion results in the formation of a sterically hindered NiL_2 complex. The addition of a third KELEX 100 molecule to the complex, although increasing the steric hindrance, would displace few solvating molecules and actually decrease the entropy of the ligand molecule in solution. The loss of ligand entropy is larger than the gain in entropy due to the release of the solvent molecules and hence the entropy change for the third step of complexation is negative.

$T\Delta S_2 < T\Delta S_1$ for both ligands with both $T\Delta S_1$ and $T\Delta S_2$ being smallest for KELEX 100. This has been also observed for the complexation of KELEX 100 with the Pb(II) and Cd(II) ions and has been explained on the basis of steric effects (see Sections 7.4 and 7.5).

Table 7.10

Stepwise thermodynamic parameters of complex formation for Ni(II) with KELEX 100 and related ligands. All data is at 25.00°C and 0.1 mol dm⁻³ ionic strength. (8HQ = 8-hydroxyquinoline.)

Ligand	Percent dioxane (v/v)	$\Delta G_1/$ kJ mol ⁻¹	$\Delta G_2/$ kJ mol ⁻¹	$\Delta G_3/$ kJ mol ⁻¹	$\Delta H_1/$ kJ mol ⁻¹	$\Delta H_2/$ kJ mol ⁻¹	$\Delta H_3/$ kJ mol ⁻¹	$T\Delta S_1/$ kJ mol ⁻¹	$T\Delta S_2/$ kJ mol ⁻¹	$T\Delta S_3/$ kJ mol ⁻¹	Reference
KELEX 100	75	-56.60	-56.42	-25.84	-35.66 (2.41)	-47.20 (3.69)	-51.88 (10.4)	19.94	9.24	-26.05	This work
8-HQ	50	-59.90	-55.74	---	-38.91	-41.84	---	20.98	13.89	---	147
2-methyl-8HQ	50	-51.12	-45.53	---	-20.92	-29.71	---	30.19	15.82	---	147
4-methyl-8HQ	50	-60.25	-56.54	---	-39.33	-37.24	---	20.92	19.31	---	147
5-sulphonic-8HQ	50	-58.31	-51.52	---	-30.54	-35.98	---	27.77	15.52	---	147

Table 7.11

Cumulative thermodynamic parameters of complex formation for Ni(II) with KELEX 100 and related ligands. All data is at 25.00°C and 0.1 mol dm⁻³ ionic strength. (8HQ = 8-hydroxyquinoline.)

Ligand	Percent dioxane (v/v)	$\Delta G_{011}/$ kJ mol ⁻¹	$\Delta G_{012}/$ kJ mol ⁻¹	$\Delta G_{013}/$ kJ mol ⁻¹	$\Delta H_{011}/$ kJ mol ⁻¹	$\Delta H_{012}/$ kJ mol ⁻¹	$\Delta H_{013}/$ kJ mol ⁻¹	$T\Delta S_{011}/$ kJ mol ⁻¹	$T\Delta S_{012}/$ kJ mol ⁻¹	$T\Delta S_{013}/$ kJ mol ⁻¹	Reference
KELEX 100	75	-56.60	-113.02	-138.86	-35.66 (2.41)	84.85 (4.41)	-134.73 (11.3)	19.94	29.2	3.13	This work
8HQ	50	-59.90	-115.64	---	-38.91	-80.75	---	20.98	34.9	---	147
2-methyl-8HQ	50	-51.12	-96.65	---	-20.92	-50.63	---	30.19	46.0	---	147
4-methyl-8HQ	50	-60.25	-116.79	---	-39.33	-76.57	---	20.92	40.2	---	147
5-sulphonic-8HQ	50	-58.31	-109.83	---	-30.54	-66.52	---	27.77	43.3	---	147

The cumulative enthalpy change was more favourable (i.e. more negative) and the entropy change was most favourable (i.e. less positive) for formation of the NiL_2 complex. However, the stabilities of KELEX 100 complexes and the substituted 8-hydroxyquinolines complexes are, within experimental error, quite similar to each other.

7.7 Discussion of thermodynamic parameters

Table 7.12 shows the stepwise thermodynamic parameters of the complexation of KELEX 100 with the various metal ions studied in this work. Table 7.13 lists the cumulative thermodynamic parameters for the complexation reactions.

The reaction heats are successively more exothermic for each metal ion studied. This has been explained by the increasing tendency of the metal ion to bond covalently after its charge has been partially neutralized by the addition of the first ligand molecule (see Section 7.4).

The cumulative enthalpy changes for the formation of ML_2 complexes decrease in the following order:



The enthalpy of complexation with Cd(II) is least favourable and is in agreement with Martinez-Garzon *et al.* [156] who studied the complexation of some metal ions with substituted pyrimidines and found that all reactions were exothermic except for Cd(II).

This is the same order as that observed by Gutnikov *et al.* [147] for the enthalpies of formation of the ML_2 complex of 8-hydroxyquinoline and its derivatives for several metal ions:

Table 7.12

Stepwise thermodynamic parameters of complex formation for Pb(II), Cd(II) and Ni(II) with KELEX 100. All data is at 25.00°C, 0.1 mol dm⁻³ ionic strength and in 75% (v/v) 1,4-dioxane.

Metal	$\Delta G_1/$ kJ mol ⁻¹	$\Delta G_2/$ kJ mol ⁻¹	$\Delta G_3/$ kJ mol ⁻¹	$\Delta G_4/$ kJ mol ⁻¹	$\Delta H_1/$ kJ mol ⁻¹	$\Delta H_2/$ kJ mol ⁻¹	$\Delta H_3/$ kJ mol ⁻¹	$\Delta H_4/$ kJ mol ⁻¹	T $\Delta S_1/$ kJ mol ⁻¹	T $\Delta S_2/$ kJ mol ⁻¹	T $\Delta S_3/$ kJ mol ⁻¹	T $\Delta S_4/$ kJ mol ⁻¹
Pb(II)	-66.47	-50.66	---	---	-26.68	-49.02	---	---	39.78	1.64	---	---
Cd(II)	-62.02	-47.47	---	42.33	-26.56	-34.68	---	-45.97	35.46	12.78	---	-88.30
Ni(II)	-56.60	-56.42	-25.84	---	-36.66	-47.20	-51.88	---	19.94	9.24	-26.05	---

Table 7.13

Cumulative thermodynamic parameters of complex formation for Pb(II), Cd(II) and Ni(II) with KELEX 100. All data is at 25.00°C, 0.1 mol dm⁻³ ionic strength and in 75% (v/v) 1,4-dioxane.

Metal	$\Delta G_{011}/$ kJ mol ⁻¹	$\Delta G_{012}/$ kJ mol ⁻¹	$\Delta G_{013}/$ kJ mol ⁻¹	$\Delta G_{-112}/$ kJ mol ⁻¹	$\Delta H_{011}/$ kJ mol ⁻¹	$\Delta H_{012}/$ kJ mol ⁻¹	$\Delta H_{013}/$ kJ mol ⁻¹	$\Delta H_{-112}/$ kJ mol ⁻¹	T $\Delta S_{011}/$ kJ mol ⁻¹	T $\Delta S_{012}/$ kJ mol ⁻¹	T $\Delta S_{013}/$ kJ mol ⁻¹	T $\Delta S_{-112}/$ kJ mol ⁻¹
Pb(II)	-66.47	-117.13	---	---	-26.68	-75.71	---	---	39.78	41.42	---	---
Cd(II)	-62.02	-109.49	---	-67.16	-26.56	-61.25	---	-107.22	35.46	48.24	---	-40.06
Ni(II)	-56.60	-113.02	-138.86	---	-36.66	-83.85	-135.73	---	19.94	29.18	3.13	---



This trend was also found by Charles [157] who studied the thermodynamics of 8-hydroxyquinoline precipitation where two molecules of 8-hydroxyquinoline reacted with a divalent metal ion. Several factors affect the enthalpy of formation in the systems Charles studied, viz. (i) the strength of the metal-ligand bonds, (ii) degree of hydration of the solid chelates, and (iii) magnitude of intermolecular forces in the solid compound. The degree of hydration was not measured by Charles but the compounds were reported to precipitate as dihydrates and are also isomorphous [158,159]. It is expected that for a series of isomorphous compounds the enthalpy of formation will vary in some regular manner with the nature of the metal. Thus a variation in ΔH would appear to reflect mainly a change in the bond strength of the metal-ligand bonds.

The stepwise entropy changes for the complexation reactions are all positive except for the relatively unstable ternary cadmium hydroxo complex and the NiL_3^- species. This may be due to the increased disorder caused by the desolvation processes of metal ions and ligands, which are much greater than the increase in order taking place in the complexation reactions.

There is a substantial decrease in entropy in successive steps of complexation, i.e. the values of $T\Delta S_2$ are much less positive than for $T\Delta S_1$. This behaviour has also been observed with the complexation of some diamines [160] and has been explained as follows:

On complex formation, solvating molecules on the metal ions and ligands are released, thus making a positive contribution to the entropy change. This positive contribution is partially offset by the loss of ligand entropy on the formation of the chelate ring. For the first step of complex formation, the former contribution to the entropy is greater than the latter and so it is positive. The addition of a second ligand to the metal ion causes a dielectric screening of

the metal ion, which in turn results in a decrease in the interaction with the solvent. Thus, on the addition of a second chelating ligand, fewer solvent molecules will be released and the loss of ligand entropy exceeds the contribution made by the release of solvent molecules.

However, in the study of diamines it was found that the entropy change for the second step of complexation was much lower than that determined for this work (in fact, it was negative). This is reasonable since the diamine complexation was studied in an aqueous medium of high dielectric constant where there would be more effective dielectric screening of the metal ion and hence a greater loss of entropy. The decrease in entropy for each successive step in complexation seems typical of several metal-ligand systems, especially where chelates are formed, and is partially attributed to the above statistical effects [161,162].

Gutnikov *et al.* [147] found that successive heats and entropies show a general trend towards somewhat more negative values. These are opposing contributions to the stability of the complexes where the enthalpy change favours stability and the entropy change decreases stability. This is in agreement with the results found for this work. In Gutnikov's work, however, the compensation is not perfect and the successive formation constants decrease by about one log unit because of greater entropy change, i.e. the entropy is the dominant factor.

The stepwise enthalpy and entropy changes were favourable for the formation of the ML^+ and ML_2 complexes of KELEX 100 and all the metal ions studied, i.e. an increase in entropy and a decrease in enthalpy. The relative magnitudes of these effects determined the order of stability of the different metal-ligand complexes.

Figure 7.5 shows that there is a larger entropy ($T\Delta S_1$) contribution to the formation of the ML^+

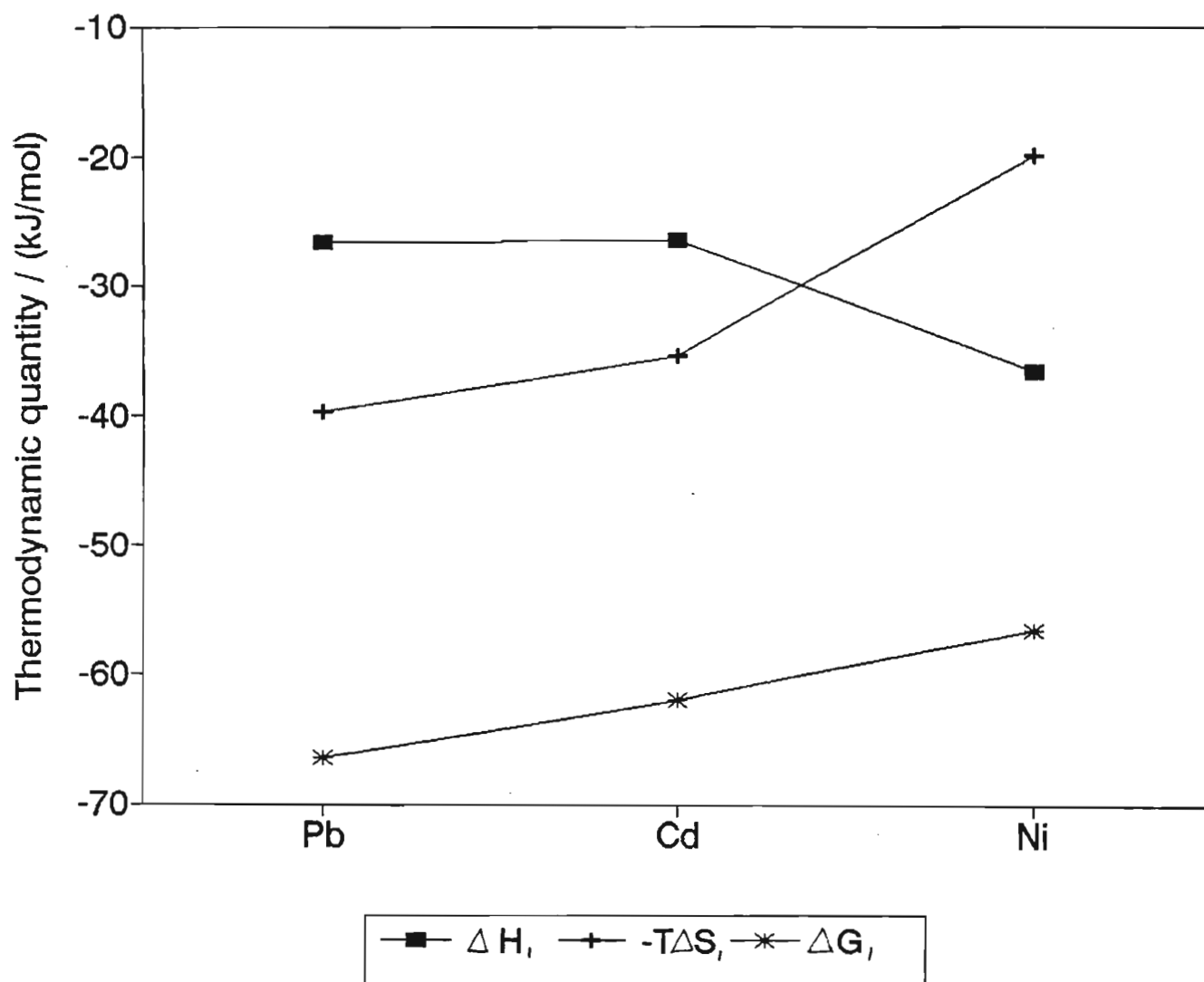


Figure 7.5 Stepwise thermodynamic parameters for the formation of the ML^+ complex of KELEX 100 with various metal ions measured at 25.00°C, in 75% (v/v) 1,4-dioxane and at an ionic strength of 0.1 mol dm^{-3} .

complex of Pb(II) and Cd(II) and a greater enthalpic contribution for Ni(II).

In the case of the stepwise formation of the ML_2 complex from the ML^+ complex, there is a much larger enthalpic contribution to the complex stability for all three ions. (See Figure 7.6.)

The cumulative thermodynamic parameters for the formation of the ML_2 complex are shown in Figure 7.7. It is seen that the cumulative enthalpic contribution (ΔH_{012}) exceeds the entropic contribution ($T\Delta S_{012}$) to the magnitude of the Gibbs free energy (ΔG_{012}) and hence is the driving force for complex stability. However, in the case of the Cd(II) ion, the enthalpy exceeds the entropy change by a relatively small value ($13.147 \text{ kJ mol}^{-1}$). It can therefore be concluded that the stability of the CdL_2 complex is due to both favourable enthalpy and entropy changes.

The effects of steric hindrance, size of the metal ion and the nature of the metal ion on the thermodynamic parameters of complexation will now be discussed.

7.7.1 Effect of steric hindrance

In general it has been observed that the reactions of KELEX 100 are more exothermic than those with 8-hydroxyquinoline, albeit at different 1,4-dioxane contents. However, this is in keeping with the expectation of greater exothermicity with an increase in 1,4-dioxane content as shown for the heats of protonation (see Section 7.3). Steger [154] found that the formation of MnL_2 , NiL_2 and ZnL_2 complexes are all more exothermic at higher 1,4-dioxane content for 8-hydroxyquinoline-5-sulphonic acid. This also is in partial agreement with the prediction that the increase in stability of complexes with an increase in organic content is due to enthalpy

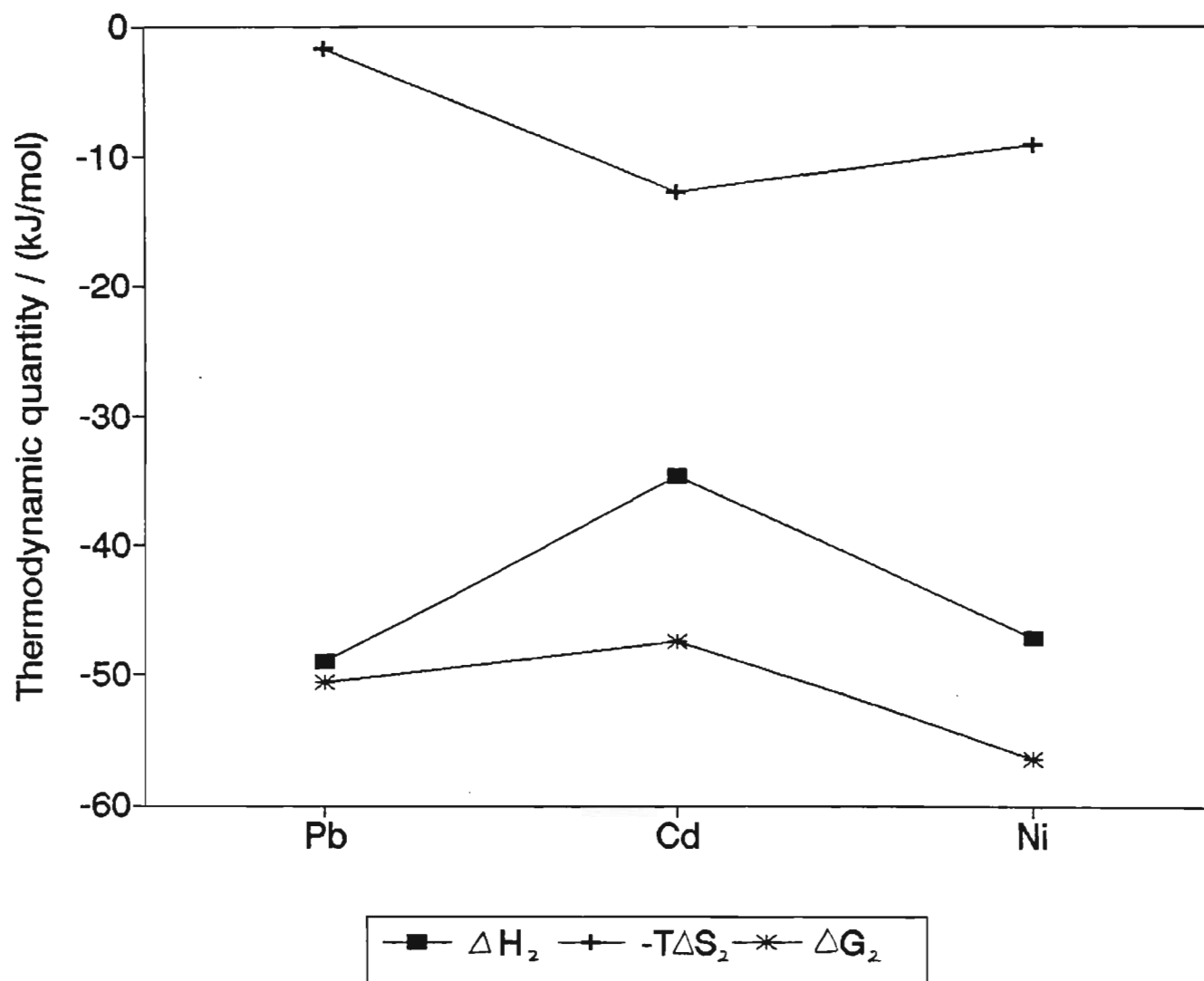


Figure 7.6 Stepwise thermodynamic parameters for the formation of the ML_2 complex of KELEX 100 with various metal ions measured at 25.00°C, in 75% (v/v) 1,4-dioxane and at an ionic strength of 0.1 mol dm^{-3} .

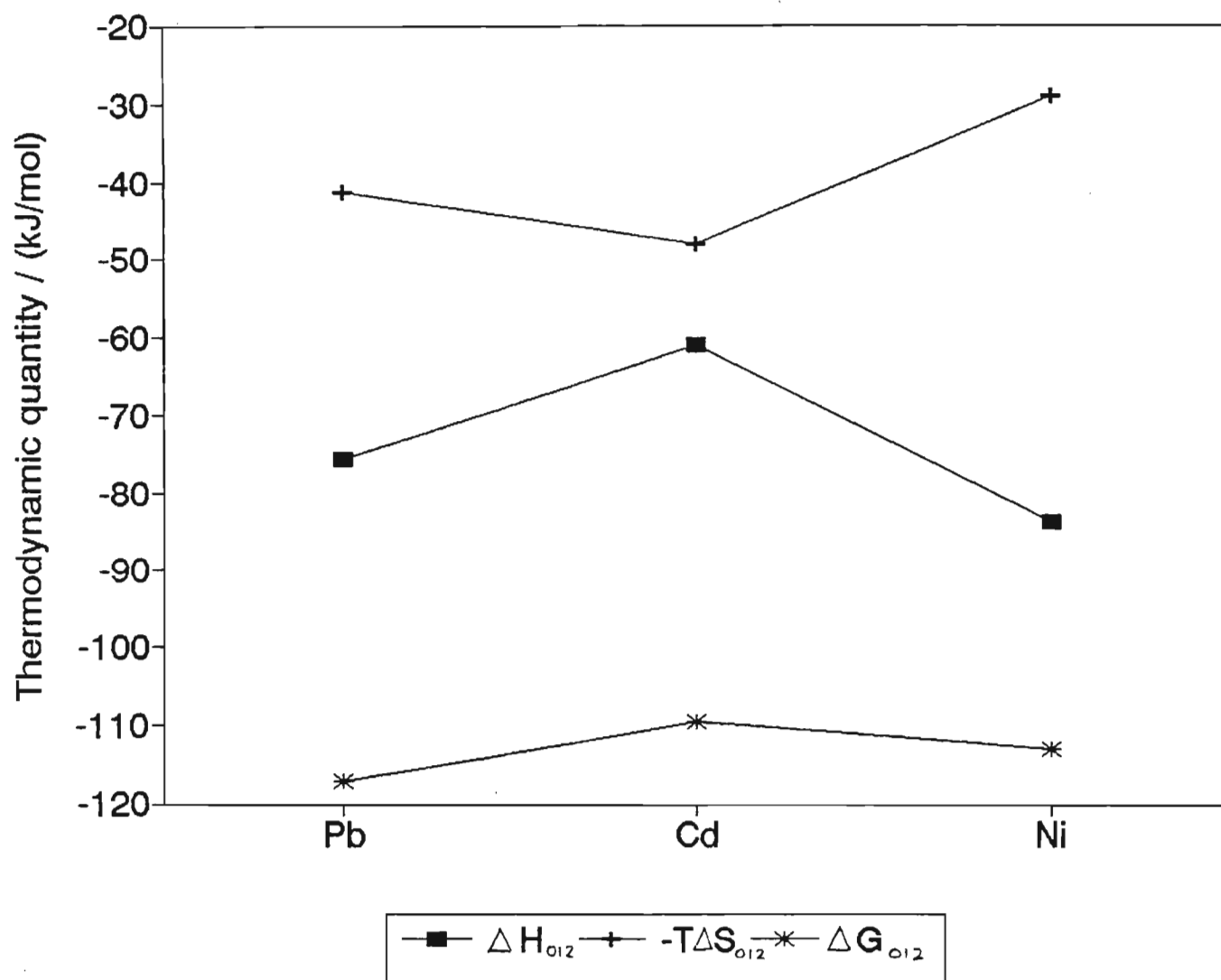


Figure 7.7 Cumulative thermodynamic parameters for the formation of the ML_2 complex of KELEX 100 with various metal ions measured at 25.00°C, in 75% (v/v) 1,4-dioxane and at an ionic strength of 0.1 mol dm^{-3} .

rather than entropy changes [155].

Table 7.14 shows the cumulative entropy changes ($T\Delta S_{012}$) for the formation of ML_2 complexes of KELEX 100 and 8-hydroxyquinoline derivatives. The cumulative entropy changes for the complexation of KELEX 100 with Pb(II) and Cd(II) are more positive than with 8-hydroxyquinoline whereas for Ni(II) the entropy change is less positive.

The increase in cumulative entropy for Pb(II) agrees with the higher entropy values measured by Gutnikov *et al.* [147] for the hindered 2- and 4-methyl-substituted 8-hydroxyquinolines. In fact, the entropy difference for KELEX 100 compared with 8-hydroxyquinoline (5.66 kJ mol^{-1}) is very similar to that for the 2-methyl- (4.92 kJ mol^{-1}) and 4-methyl (5.63 kJ mol^{-1}) derivatives. Since the entropy change is only slightly affected by the increase in 1,4-dioxane content as shown by Steger [154], the data suggests that, for Pb(II), the bulky alkyl substituent on KELEX 100 does not contribute significantly more than the methyl substituent to the entropy change. Hence steric effects are not reflected in the entropy change.

The methyl-substituted 8-hydroxyquinolines show an increased entropy change compared to 8-hydroxyquinoline, but the entropy change for the complexation of KELEX 100 and Ni(II) is less positive. This effect is difficult to explain although it has been observed by Corsini *et al.* [163] that, for 2-substituted 8-hydroxyquinolines, the Ni(II) ion is more susceptible to steric hindrance effects than other ions and this contradicts the normal stability sequence of metal ions, i.e. while the order of stability for 8-hydroxyquinoline is: $\text{Cu} > \text{Ni} > \text{Co} > \text{Zn}$, the order of stability for 2-substituted 8-hydroxyquinolines is $\text{Cu} > \text{Zn} > \text{Co} > \text{Ni}$. In this work, the greater steric hindrance due to the large size of the KELEX 100 ligand may account for the smaller entropy changes of formation for the Ni(II)-KELEX 100 complexes.

Table 7.14

Cumulative entropies (in kJ mol^{-1}) of ML_2 complex formation for Pb(II), Cd(II) and Ni(II) with KELEX 100 and related ligands. All data is at 25.00°C and 0.1 mol dm^{-3} ionic strength. All values are reported at a composition of 50% (v/v) 1,4-dioxane except for KELEX 100 which is in 75% (v/v) 1,4-dioxane. (8HQ = 8-hydroxyquinoline.)

Metal	KELEX 100	8HQ	2-methyl-8HQ	4-methyl-8HQ
Pb(II)	41.42	35.76	40.08	41.39
Cd(II)	48.24	38.29	-	-
Ni(II)	29.18	34.87	45.89	40.23

Several workers have carried out a thorough thermodynamic study of the stability of ethylenediaminetetraacetic acid (EDTA) complexes and these results are summarised by Dwyer *et al.* [163]. In the case of EDTA both the enthalpy and entropy are favourable for complexation with the three metal ions studied here. In the case of Cd(II), it was found that the entropic and enthalpic contributions to the stability of the complex were approximately equal and, in the case of the Pb(II) ion, the enthalpy change was the greater contributor to the Gibbs free energy, which is the same as that observed for this work.

The substantial entropy contributions to chelate stability were generally ascribed to the removal of solvating water molecules from hydrated ions. However, Kurihara *et al* [165] showed that this effect is not only peculiar to aqueous media since the release of dimethylformamide molecules from a coordination sphere into a bulk structureless solvent also leads to a larger entropy gain. Arhland [166,167] showed that this behaviour is generally observed for aprotic solvents. On this basis, it is possible to explain results obtained in the 75% (v/v) 1,4-dioxane medium used in this work.

7.7.2 Effect of ion size

The thermodynamics of complexation between metal ions and ligands usually show some dependence on the relative sizes of the two reactants. In this work a single ligand was used and it was expected that some of the thermodynamic parameters would depend on the size of the metal ion studied.

The ionic radii of each metal ion used in this work were calculated by Shannon [168] and are shown in Table 7.15. The coordination number of each metal ion was assumed to be six.

Table 7.15

Effective ionic radii calculated by Shannon [168] of metal ions used in this work. Ions have been arranged in order of increasing ionic radius.

Metal ion	Coordination number	Ionic radius/Å
Ni ²⁺	VI	0.69
Cd ²⁺	VI	0.95
Pb ²⁺	VI	1.19

Figure 7.8 shows the variation of the stepwise enthalpy and entropy change for the formation of the ML^+ complex. The stepwise entropy ($T\Delta S_1$) increases with an increase in ionic radius. This is more marked in the case of the Ni(II) ion. The Ni(II) has a high charge density and is strongly solvated, i.e. has a large hydration sphere. The reaction of the ion with the first ligand displaces some of the solvating molecules which results in an increase in entropy. On account of its high charge density, however, it will still be fairly strongly solvated and hence the entropy increase would be less than that for Pb(II) or Cd(II). The Pb(II) has the lowest charge density and will probably be poorly solvated and thus lose most of its solvating molecules. Hence it exhibits the largest entropy change.

The stepwise enthalpy (ΔH_1) decreases with an increase in ionic radius, i.e. becomes more exothermic. The loss of solvating molecules from a hydration sphere is an endothermic process. In the case of Ni(II) where less molecules are lost from the hydration sphere, it is expected that there is a smaller endothermic contribution to the enthalpy and hence the reaction is more exothermic.

Figure 7.9 shows the variation of the stepwise enthalpy and entropy changes for the formation of the ML_2 complex. There is no linear correlation of the stepwise parameters with ionic radius. However, it is observed that there is a very small increase in entropy (i.e. close to zero) for the stepwise formation of the ML_2 complex of lead. This agrees with the assumption above that the Pb(II) ion is poorly solvated after the formation of the ML^+ complex. This explains the more exothermic reaction since there is no endothermic contribution to the enthalpy.

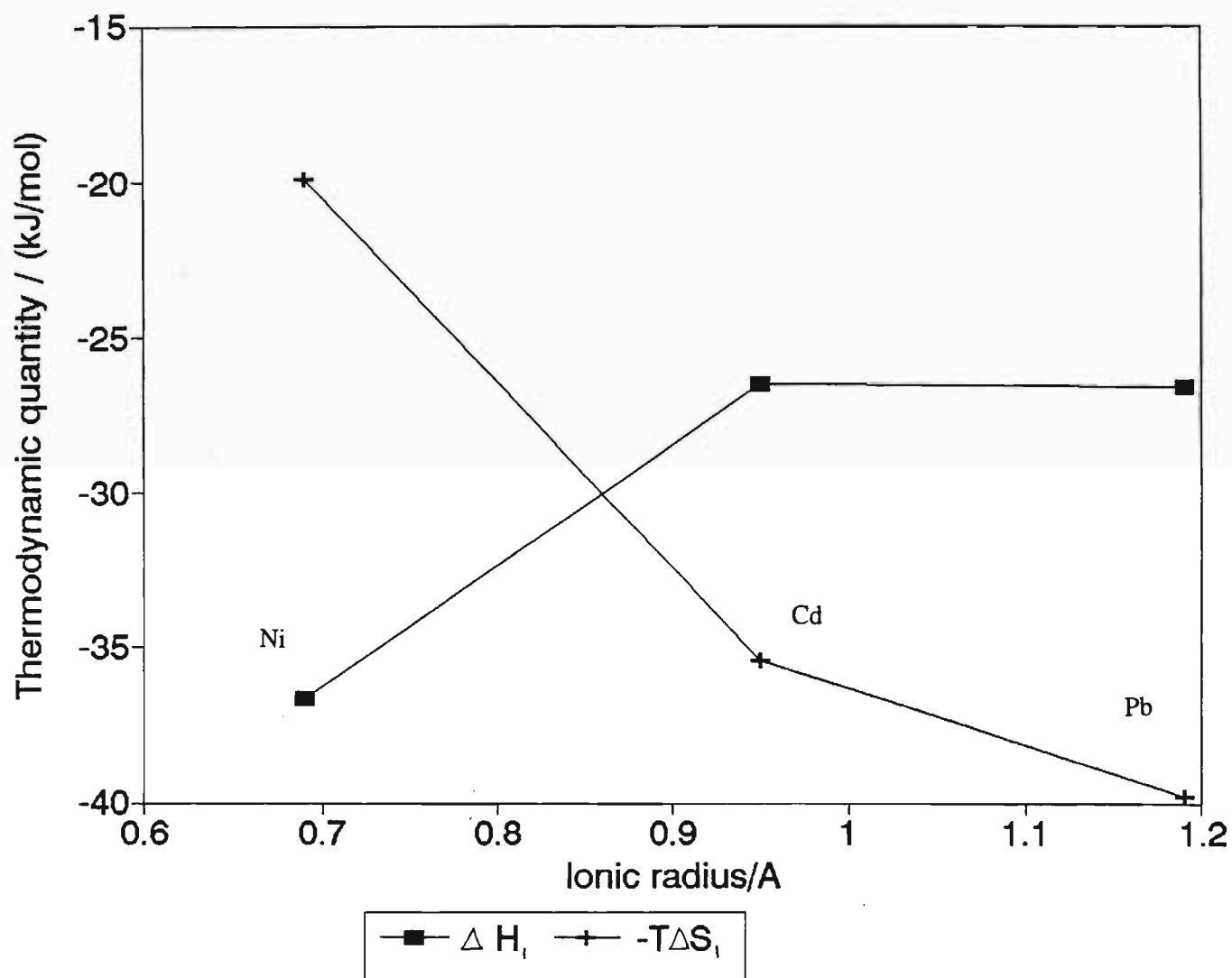


Figure 7.8 Variation of the stepwise enthalpy and entropy changes for the formation of the ML^+ complex with the radius of the metal ion.

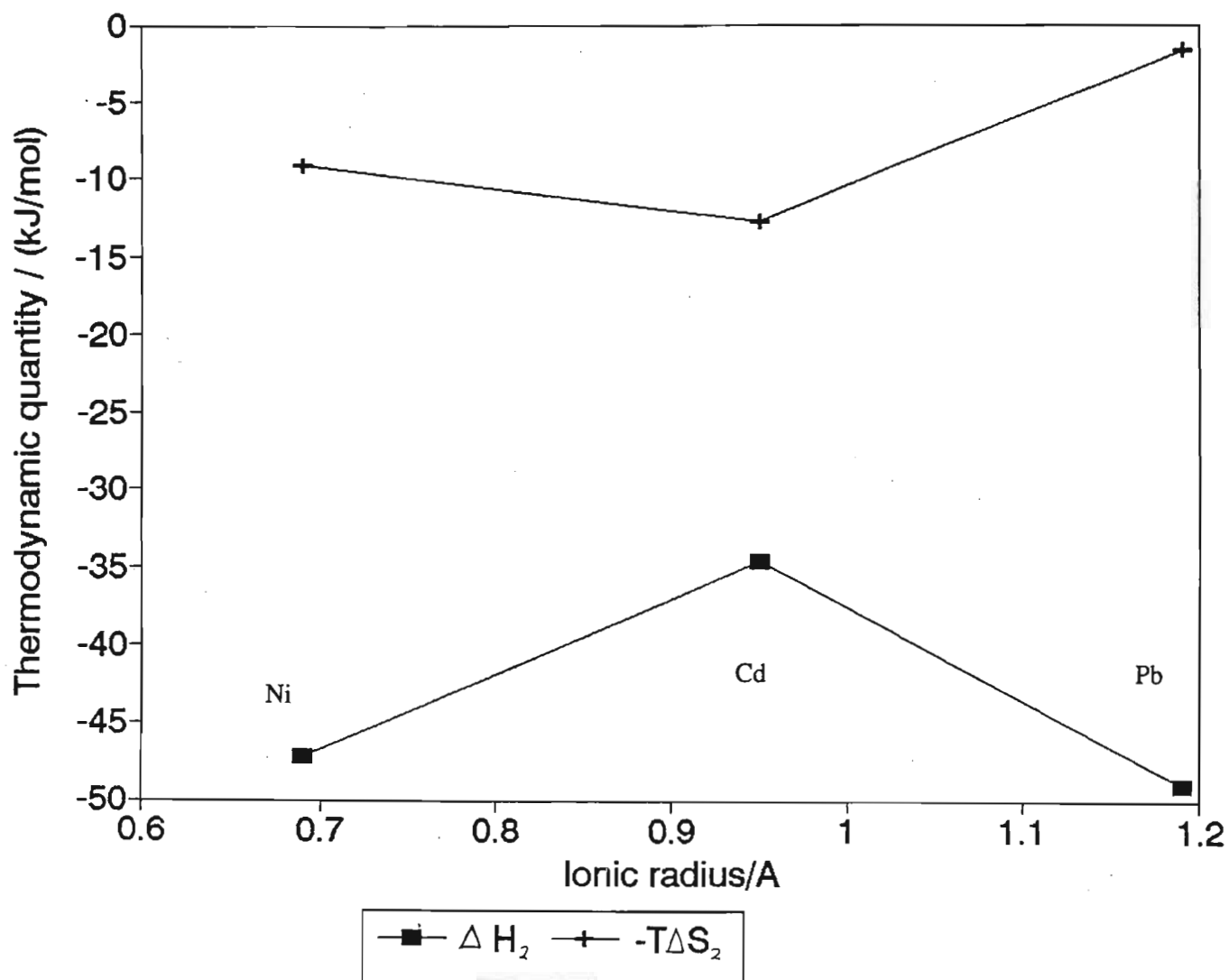


Figure 7.9 Variation of the stepwise enthalpy and entropy changes for the formation of the ML_2 complex with the radius of the metal ion.

The magnitude of the stepwise enthalpies for the formation of the ML_2 complexes (ΔH_2) are much larger than the corresponding entropies. Figure 7.10 shows the variation of the cumulative enthalpies and entropies with ionic radius. The domination of the ΔH_2 and $T\Delta S_2$ terms to the cumulative parameters is reflected in the similarity of Figures 7.9 and 7.10.

The size of the Cd(II) ion is intermediate between that of Ni(II) and Pb(II) and the stepwise and cumulative enthalpies and entropies would also be expected to be intermediate between those of Ni(II) and Pb(II). However, this is not observed and it is likely that there are other properties of the metal ion that influence the thermodynamics of complexation. The nature of the bond formed by the metal ion with particular ligands is an important factor to consider in this instance.

7.7.3 Effect of softness of the metal ion

Metal ions are known to have particular preferences for certain ligands in aqueous solution. The Hard and Soft Acid-Base (HSAB) theory developed from attempts to correlate a large amount of experimental observations. Pearson [88] qualitatively classified the metal ions as 'hard' or 'soft' Lewis acids depending on their size, charge density and polarisability. An ion was termed 'hard' if it was small, had a high charge and was not easily polarisable. 'Soft' metal ions were large, had low charge and were easily polarisable. Ligands were also classified as 'hard' or 'soft' Lewis bases depending on whether the donor atoms in the ligand were 'hard' or 'soft'. The KELEX 100 ligand is considered to be a 'hard' ligand on account of the N and O donor atoms which are classified as 'hard'. Several attempts have been made to quantitatively establish scales of softness or hardness. While some have been successful in correlating a set of experimental observations, no classification system has been found to

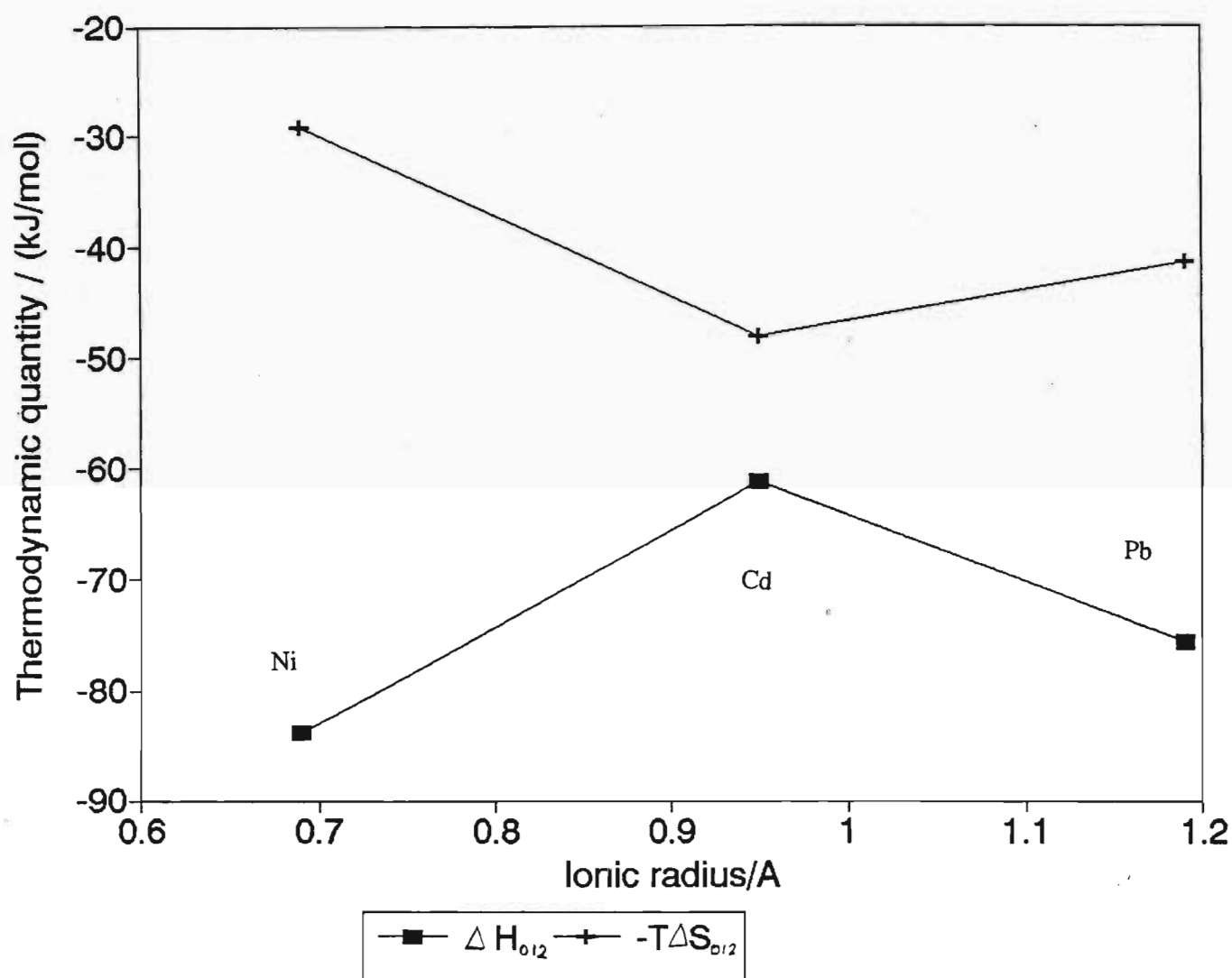


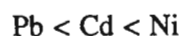
Figure 7.10 Variation of the cumulative enthalpy and entropy changes for the formation of the ML_2 complex with the radius of the metal ion.

be universally applicable. It has been observed that, though the HSAB theory may be useful in many instances, it is difficult to use it as a basis for explaining bonding and stabilities in systems where the softness parameters are not accurately quantified. This may be less of a problem with ions that are known to display behaviour typical of hardness or softness. However, in systems where the ions are borderline cases, the theory becomes difficult to apply. This problem is further complicated by the various scales of softness proposed which differ amongst themselves.

For example, the α parameter of softness defined by Yamada *et al.* [169] gives the following order of softness [169]:



whereas the σ parameter of Arhland [170] gives the following order:



It is clearly seen that Pb can be regarded either as the softest or the hardest of the three metal ions and a particular scale of softness can be invoked to justify a particular set of results.

However, the qualitative system of classification on the basis of experimental observations by Pearson [88] and Williams *et al.* [171] lists the Cd(II) ion as the softest of the three metal ions studied. The interaction of the soft Cd(II) ion and the hard KELEX 100 ligand thus results in a weak complex. The formation of this weak complex may account for the small stepwise and cumulative enthalpy changes. Another factor that may affect the thermodynamics of complexation but was not studied in this work is the effect of the geometry of the metal-ligand complex. Nakabayashi *et al.* [172] studied the complexation of metal ions with 8-

quinolinethiol in dimethylsulphoxide and found that the enthalpies of formation ML_2 divided the metal ions into two groups, depending on the geometry of the ligand complex. Each group was linearly related to the α -parameter of softness. The Cd(II) ion did not lie on the same line because it was considered to complex in an a tetrahedral configuration.

It is clear that several factors influence the thermodynamics of complexation between metal ions and ligands. Some of these factors were not investigated in this work and this makes it difficult to interpret the results and to explain them fully. However, it is possible to make some tentative conclusions.

7.8 Conclusions

The stepwise enthalpies of formation were successively more exothermic for the metal ions studied. This has been explained by the increasing tendency of the metal ion to bond covalently after its charge has been partially neutralized by the addition of the first ligand molecule.

There is a decrease in stepwise entropy in successive steps in complexation. This is probably due to a greater degree of desolvation of the metal ion in the first step than in the second step of complexation.

The cumulative entropies and enthalpies of formation of both the ML^+ and the ML_2 complexes were favourable, i.e. the complexation reactions were accompanied by a decrease in enthalpy and an increase in entropy. Thus both enthalpy and entropy were the driving forces behind the formation of complexes. The entropy change was the greater contributor

to complex stability for the formation of the ML^+ complexes of the Cd(II) and Pb(II) ions. However, the enthalpy changes contributed more to the stability of the ML_2 complexes for all the metal ions studied. For the Cd(II) ion, the $T\Delta S_{012}$ and the ΔH_{012} contributions were not very different, indicating that the entropy and enthalpy contribute equally to the stability of the cadmium(II) complexes. The smaller enthalpy contribution for the ML_2 complex for the Cd(II) ion is possibly due to the formation of a weak complex between the 'soft' Cd(II) ion and the 'hard' KELEX 100 ligand. However, the value of ΔH_{012} is much larger than $T\Delta S_{012}$ for the Pb(II) and Ni(II) ions.

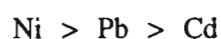
The entropies of formation of $Pb(KELEX\ 100)_2$ complexes are similar for other methyl-substituted hydroxyquinolines, indicating that the entropies are independent of steric effects for the Pb(II) ion. For the $Ni(KELEX\ 100)_2$ complex, however, the entropy change is much smaller than that of other substituted hydroxyquinolines. This is possibly due to the fact that the smaller Ni(II) ion is more susceptible to steric hindrance.

The enthalpies of formation of the ML^+ complexes of KELEX 100 are similar to those of the substituted 8-hydroxyquinolines. However, for the ML_2 complexes, the enthalpies of formation are slightly higher than the substituted 8-hydroxyquinolines. However, this is expected to be due to the increase in 1,4-dioxane content and not steric effects.

The entropies of the first complexation step were found to increase with an increase in ionic radius. This was thought to be due to the loss of fewer solvent molecules on complexation from the smaller metal ions which were thought to bind the solvating molecules more strongly.

The enthalpies of the first step of complexation were found to be less exothermic with an increase in ionic radius of the metal ion. This may be due to a larger endothermic contribution from the desolvation process which occurred to a lesser extent for the smaller Ni(II) ion.

The cumulative enthalpies of formation of the ML_2 were found to increase (i.e. more exothermic) in the order:



whereas the entropies of formation of the ML_2 complex were found to increase in the order:



The smaller enthalpy change for the formation of the CdL_2 complex was thought to be due to the weak interaction between the 'soft' Cd(II) ion and the 'hard' KELEX 100 ligand. The smaller entropy change for the Ni(II) ion may be due to the solvent molecules being bound more strongly to the ion and so less are released on complexation.

No linear correlations were found between the cumulative entropies or enthalpies and the properties of the metal ion.

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APPENDIX I

Listing of the GWBASIC program METAL.

```
10 CLS
20 PRINT: PRINT
30 PRINT "(01/11/94 - Terence Singh)"
40 PRINT : PRINT
50 PRINT " This program allows you to calculate the correct volumes of water,"
60 PRINT " dioxane and NaClO4 solutions to give a metal ion mixture of the correct"
70 PRINT " ionic strength"
80 PRINT : PRINT
90 PRINT
100 INPUT "What is the final volume of the mixture needed (in ml)  ",VF
110 REM *** INPUT OF VALUES OF CONSTANTS ***
120 PRINT : PRINT
130 PRINT "Enter the following variables : "
140 PRINT
150 PRINT
160 INPUT " Concentration of metal ion solution (M) : ",CH
170 INPUT " Final ionic strength of mixture (M)      : ",I
180 INPUT " Contraction factor of the mixture (M)   : ",CF
190 INPUT " Concentration of NaClO4 solution (M) : ",CN
200 INPUT " Final concentration of metal ion (M)   : ",CHF
```


APPENDIX II

Listing of the GWBASIC program DEPROT.

```
10 CLS
20 PRINT : PRINT
30 PRINT " (01/11/94 - Terence Singh)
40 PRINT : PRINT
50 PRINT " This program allows you to calculate the correct volumes of water,"
60 PRINT " dioxane and NaClO4 solutions to give a mixture of the correct ionic strength"
70 PRINT : PRINT
80 PRINT " and not only that, it also shows one how much base and KELEX 100 to add to "
90 PRINT " deprotonate it completely"
100 PRINT
110 INPUT "What is the final volume of the mixture needed (in ml) ",VF
120 REM *** INPUT OF VALUES OF CONSTANTS ***
130 PRINT : PRINT
140 PRINT "Enter the following variables :"
150 PRINT
160 PRINT
170 INPUT " Concentration of NaOH solution (M)           :",CB
180 INPUT " Final ionic strength of mixture (M)           :",I
190 INPUT " Contraction factor of the mixture             :",CF
200 INPUT " Concentration of Kelex 100 in dioxane (M)      :",CK
```


APPENDIX III

Listing of the GWBASIC program DIOX.

```
10 CLS
20 PRINT " This program allows you to calculate the correct volumes of water,"
30 PRINT " dioxane and NaClO4 solutions to give a mixture of the correct ionic strength"
40 PRINT
50 INPUT "What is the final volume of the mixture needed (in ml) ",VF
60 REM *** INPUT OF VALUES OF CONSTANTS ***
70 PRINT : PRINT
80 PRINT "Enter the following variables :"
90 PRINT
100 PRINT
110 INPUT " Percentage of dioxane-water mixture      : ",P
120 INPUT " Final ionic strength of mixture(M)      : ",I
130 INPUT " Contraction factor of the mixture       : ",F
140 INPUT " Concentration of NaClO4 solution(M)     : ",C
150 REM *** CALCULATION OF DUMMY VARIABLES ***
160 DI = (1/F) - (1/C)
170 D2 = (100 - P)/100
180 D3 = P/(100 - P)
190 D4 = (1/C) * D3
200 REM *** CALCULATION OF CONSTITUENT SOLUTION VOLUMES ***
```

```

210 REM *** VW = VOLUME OF WATER ***
220 REM *** VN = VOLUME OF NaClO4 SOLUTION ***
230 REM *** VD = VOLUME OF DIOXANE ***
240 REM *** VF = TOTAL VOLUME NEEDED ***
250 VN = (1/C) * VF
260 VW = D2 * (D1 - D4) * VF
270 VD = (D1 - D2 * (D1 - D4)) * VF
280 REM *** DISPLAY OF RESULTS ***
290 PRINT : PRINT
300 PRINT " To make";VF; "ml of a";P;"% dioxane mixture, the ff. volumes are needed : "
310 PRINT
320 PRINT " Volume of water           " ;VW; " ml"
330 PRINT " Volume of NaClO4 solution    " ;VN; " ml"
340 PRINT " Volume of dioxane               " ;VD; " ml"
350 PRINT : PRINT
360 END

```