STUDIES ON
COMPLEXING AND ION PAIRING
IN SOLUTION

A Thesis
Submitted to the University of Glasgow
for the degree of
DOCTOR OF PHILOSOPHY

by

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SUMMARY

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Studies have been made on the association in aqueous solution between divalent alkaline earth metal ions and the anions of N-Methyliminodiacetic acid and glycine.

The thesis is divided into three parts. Part I describes a Nuclear Magnetic Resonance study of magnesium, calcium, strontium and barium N-Methyliminodiacetate complexes. Protonation schemes have been established for these complexes and evidence for binding sites obtained from variations in the resonance positions of the non-labile protons on the ligand. The results have been discussed and comparisons with other similar systems have been made.

Part II deals with the determination of the dissociation constants for glycine and for the mono-protonated form of N-methyliminodiacetic acid. Association constants for the divalent magnesium, calcium, strontium and barium mono- and di-N-methyliminodiacetate complexes and for the magnesium mono-glycinate complex have also been obtained. All measurements were made at 25°C. and a constant ionic strength of 0.1M using a cell incroporating a pair of glass electrodes and a 0.1M calomel electrode. The activity coefficient for the hydrogen ion was calculated from the Davies equation,

$$-\log f_{H^+} = AZ^2\left(\frac{I^{\frac{1}{2}}}{1 - I^{\frac{1}{2}}} - 0.3I\right)$$

A calorimetric investigation, at 25°C. and an ionic

strength of 0.1M, of the heats of formation, ΔH_I, of the mono-methyliminodiacetate complexes of magnesium, calcium, strontium and barium and of the 2:1 complexes of this anion with magnesium and calcium is described in Part III. Also included in this section are ΔH_I values for the magnesium and calcium monoglycinate complexes. Twin adiabatic calorimeters were used which employed as sensing elements a pair of matched thermistors which were incorporated in two arms of a Wheatstone bridge. Variations in structure, coordination number, degree of hydration and steric properties are discussed in terms of the thermodynamic properties of the complexes. Thermodynamic functions for the reaction,

$$\text{Metal(MIDA)}_2^{2-} + \text{EDTA}^{4-} \rightleftharpoons \text{Metal EDTA}^{2-} - 2\text{MIDA}^{2-}$$

have been derived for divalent magnesium, calcium, zinc and cadmium ions and these are discussed.

FOREWORD

The first two years of the research described in this thesis were carried out in the Physical Chemistry Department at the University of Glasgow, which is under the direction of Professor J. M. Robertson, F.R.S. and the work was completed at the State University of New York at Buffalo, (U.S.A.) under Professor G. H. Nancollas.

I am indebted to Professor Nancollas under whose supervision the entire work was performed, for his encouragement and guidance throughout my research degree course and to Dr. Helen S. Dunsmore who wrote the computer programmes. Thanks are due to the staff of both Universities for the construction and maintainance of apparatus.

I wish also to express my gratitude to the Science and Research Council and to the State University of New York at Buffalo for the award of maintainance grants which made this research possible.

Andrew C. Park.

GENERAL INTRODUCTION

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In solutions of electrolytes it is desirable to be able to characterise the species present. In the case of a solid crystal, X-ray crystallographic methods can yield absolute structures of the molecules. Unfortunately in the case of electrolyte solutions, there is no such unequivocal method available for the determination of the structures of the species present. In some cases, it is clear that the structure of the solid can be used to describe the species in solution. The similarity of the visible absorption spectra[1] of aqueous solutions of transition metal cations such as nickel (II) with those of hydrated salts, e.g. $Ni SO_4 .7H_2 O$, provides strong evidence that the ion in solution is in the same immediate environment of six octahedrally co-ordinated water molecules as in the solid hydrate. In other cases, this assumption has been shown to be unjustified. Chapman et al[2], have shown, by spectroscopic techniques, that a number of α-amino-polycarboxylic acids are present as the zwitterion form in solution while they have the "normal" acid structure in the solid. Some newer physical methods like those used by Chapman come close to yielding structures of species in solution in giving information about the sites of binding of a ligand to a metal ion and these will be discussed later.

Bjerrum[3] and others have shown that complex formation involving a metal ion and a ligand is a stepwise process which in aqueous solution can be represented by equilibria of the type,

$$M^{n+}_{aq} + A^{m-}_{aq} \rightleftharpoons MA^{(n-m)+}_{aq} \text{------------------}(1)$$

$$MA^{(n-m)+}_{aq} + A^{m-}_{aq} \rightleftharpoons MA^{(n-2m)+}_{2\ aq} \text{-----------------}(2)$$

$$\begin{array}{ccc} \vdots & \vdots & \vdots \end{array}$$

$$MA^{[n-(N-1)m]+}_{(N-1)aq} + A^{m-}_{aq} \rightleftharpoons MA^{[(n-Nm)]+}_{N\ aq}$$

where M^{n+} and A^{m-} denote the metal ion and the ligand ion respectively, $MA^{[n-(1,2,\ldots N)m]+}_{(1,2,\ldots N)}$, the various complex species formed and N, the maximum number of ligands that can bind to one metal ion. With charged ligands, A^{m-}, progressive neutralisation of the charge on the metal ion takes place and there is a smaller probability factor arising from a decrease of the number of available co-ordination sites of the metal. With bulky ligands there may also be considerable steric hindrance to the entry of successive groups.

Equilibria such as (1) can be described by an equilibrium constant, the stability constant, written,

$$K_{MA} = \frac{[MA^{(n-m)}]}{[M^{n+}]\,[A^{m-}]} \text{-----------------------}(3)$$

where square brackets denote concentrations. K_{MA} is valid at the particular temperature studied and at the ionic concentration of the solution in which it was measured. Stability constants are usually measured at constant ionic strength and can be compared only with others obtained under the same conditions of temperature and ionic strength. In order to be able to compare different systems it is desirable to obtain the thermodynamic association constant for reaction (1) given by,

$$K = \frac{\{MA^{(n-m)}\}}{\{M^{n+}\}\{A^{m-}\}} = \frac{[MA^{(n-m)}]}{[M^{n+}][A^{m-}]} \cdot \frac{f_{MA}^{(n-m)}}{f_{M}^{n+} \cdot f_{A}^{m-}} =$$

$$K_{MA} \cdot \frac{f_{MA}^{(n-m)}}{f_{M}^{n+} \cdot f_{A}^{m-}} \text{ ------------(4)}$$

where braces enclose activities and f's are the corresponding activity coefficients. For the evaluation of K, it is necessary to either calculate or eliminate the activity coefficients term. Either, K_{MA} can be calculated at a number of ionic strengths and extrapolated to zero ionic strength at which the activity coefficients become unity, or else the activity coefficients can be calculated from some suitable extension of the Debye - Huckel equation. The first of these methods is very tedious since at low constant ionic strengths it is sometimes necessary to make the experiments by a series of successive approximations in order to ensure that the ionic strength is held constant. The calculation of activity coefficients can sometimes be rendered difficult by high charges on the species and under such conditions it is advantageous to make measurements at constant ionic strength and obtain stability constants which are valid at this particular ionic strength. In order to be sure that the activity coefficients are held constant the concentrations of reacting species must be small and contribute only to a negligible extent to the total ionic strength. This is often difficult to achieve, however, especially when studying reactions between highly charged ions forming complexes with relatively low stability constants ($<10^{-3}$ litre mole^{-1}). In such cases, successive approximations must be made for I, the total ionic strength, since a knowledge of the stability constant is required before the concentrations of ionic species and their contribution to I can be calculated.

A number of methods are available for measuring association constants for the formation of complexes in solution. These can be divided broadly into two classes: (1) indirect methods in which the activity of a single ionic species in the solution is measured whose concentration is controlled by a well defined equilibrium and (2) direct methods in which the concentration of the new species, the complex, is directly indicated by a change in some property of the solution. A few of the more important methods will be discussed briefly here.

Many important ligands are anions of weak acids and are thus associated to a varying degree with hydrogen ions. Complex formation with a metal ion results in the displacement of these hydrogen ions with a subsequent reduction in pH. The measurement of pH therefore may be used to determine the association constant for the formation of the complex.

The use of an electrode reversible with respect to hydrogen ions yields hydrogen ion activity in the solution and thus it is necessary to know the activity coefficient, f_{H^+}, of the H^+ ion. In experiments at constant ionic strength, however, it is desirable to calibrate the electrodes as concentration rather than as activity probes since f_{H^+} values, even at ionic strengths as low as 0.1, cannot be reliably estimated. It is therefore preferable to calibrate the electrodes in dilute solutions of strong acid or base, adjusted to the required ionic strength with a "neutral" electrolyte such as sodium perchlorate[4,5].

A great deal of work using cells without liquid junction of the type

$$H_2(1\ \text{atm.}),\ Pt\ /\ HA,\ NaA,\ NaCl\ /\ AgCl\ /\ Ag$$

has been done by Harned and coworkers[6]. Very precise e.m.f.'s can be obtained for the calculation of dissociation constants.

The glass electrode is probably the most frequently used electrode for studies of complex formation in solution. The cells normally incorporate glass and calomel electrodes connected through a potassium chloride salt bridge. Glass electrode measurements have been used to determine the association constants for some alkaline earth monoacetates for which the extent of association is rather small[7]. The general treatment for the determination of stepwise stability constants from measurements of this type is described by Bjerrum[8], whose work in the elucidation of species present in metal ammine solutions is a classical example of the method.

Since the introduction of well-characterised organic ion - exchange resins some 20 years ago, they have found increasing applications in complex formation studies. The equilibrium established when a cation exchange resin in, say, the sodium form, NaR, is in contact with a solution containing M^{n+} ions, may be written

$$n\,NaR + M^{n+} \rightleftharpoons MR_n + nNa^{+} \text{---------------} (5)$$

and the equilibrium quotient at constant ionic strength,

$$Q = \frac{[\overline{M^{n+}}]\ [Na^{+}]}{[M^{n+}]\ [\overline{Na^{+}}]} \text{------------------------} (6)$$

where $[\overline{\ \ }]$ represents the resin-phase concentrations in mole/g. dry resin. Addition of an anion, X^{m-}, capable of complexing with M^{n+} will cause a redistribution of free M^{n+} ions between the resin and the solution by an ammount which is quantitatively related to the extent to which M^{n+} is bound by the anions. Fronaeus[9] developed a graphical solution for systems of the type $M^{2+} + X^{-}$ where M^{2+} and the first complex, MX^{+}, are taken up by the cation exchanger. By assuming that higher complexes with zero or negative charge do not take part in the exchange, he obtained association constants for the formation of the Cu(II) acetate species $CuAc^+$, $CuAc_2$, and $CuAc_3^-$ and the nickel (II) acetate complexes $NiAc^+$, and $NiAc_2$, which agree closely with potentiometric values.

The stability quotients obtained by ion-exchange methods are necessarily rather approximate owing to a lack of knowledge concerning the variation of activity coefficients with composition particularly in the resin phase. The method is useful, however, for indicating the sign of the electrical charge residing on a species in solution.

The formation of a metal complex is often accompanied by a change in the light absorption of the complex relative to that of the free metal ion or ligand. Where the new species absorbs in the visible or ultraviolet the change in the absorption spectrum can yield directly the concentration of the species[10,11]. A great advantage of the spectrophotometric method is that it can be used in very dilute solutions so that the calculation of activity coefficients is facilitated. It is also much more direct than the potentiometric or ion - exchange method and at first sight has a considerable number of advantages. However, an additional quantity, the extinction coefficient of the absorbing species is introduced so that it is sometimes difficult to separate the association constant from the extinction coefficient of the complex species.

In certain favourable cases, the halfwave potential of a metal ion is shifted to more negative values as the concentration of the associating ligand is increased. The magnitude of this shift of half wave potential can be used to calculate both the stability and the composition of the complex species in solution[12,13]. Normally, since the ionic strength of the solution is maintained at a relatively high value with neutral electrolyte to ensure that the current is purely diffusion controlled, the stability constants obtained are valid only at the particular ionic strength used. However, some studies have been made by polarographic methods[14] of systems at a series of constant ionic strengths and the results extrapolated to zero concentration in order to evaluate the thermodynamic association constants.

Other important methods that can be used include, conductivity[15,16], solubility[17,18,19], kinetic[20,21], and solvent extraction measurements[22,23]. In addition, new physical measurements such as, nuclear magnetic resonance[24], Raman spectroscopy[25], and sound absorption[26], have been used, giving in many cases, a more detailed picture of the species in solution.

The free energy change, ΔG, for a reaction such as (1) is defined by,

$$-\Delta G = RT \ln K. \text{------------------}(7)$$

To gain a better insight into the factors which control the equilibrium, it is more useful to regard the free energy change as being a consequence of the changes in heat, ΔH, and entropy, ΔS of complex formation. The three functions are related by the equation,

$$\Delta G = \Delta H - T\Delta S. \text{------------------}(8)$$

If K in equation (7) is a stability constant at a particular ionic strength then, the ΔG derived from this relationship will refer to these specific conditions of temperature and ionic strength. Consequently, the thermodynamic properties will refer to the standard states at the particular ionic strength used.

The representation of the complex formation by reaction (1) does not take into account the changes in the numbers of water molecules associated with the ions. It is therefore better written,

$$M(H_2O)_x^{n+} + A(H_2O)_y^{m-} \rightleftharpoons MA(H_2O)_z^{(n-m)+} + (x-y-z)H_2O \text{-------} (9)$$

where x, y and z are the water molecules associated with the metal, ligand and complex respectively. The enthalpy change accompanying complex formation is a measure of the numbers and strengths of bonds made and broken during the reaction. The entropy change is a measure of the change of randomness and the driving force is the tendency for the system to go to the most probable, that is the most random state. Favourable ΔG values may be assisted by negative enthalpy or positive entropy changes. There are endothermic reactions which are made possible by favourable entropy changes, and there are exothermic reactions which do not take place because of unfavourable entropy changes.

If we consider complex formation as represented by equation (9), it is seen that the number of species is reduced during the formation of the complex. The change would therefore be expected to be accompanied by a moderately large and negative entropy reflecting the disappearance of one of the species. However, the free ions are associated to varying degrees with water molecules and the overall complex formation is accompanied by release of some of these water molecules. Since the water molecules bound to cations or anions are highly oriented, an increase in entropy will result when they are released from this type of restraint. Thus association reactions involving small highly charged cations take place with relatively large positive values of ΔS. A large cation such as Tl^+, on the other hand, which has a comparatively high aqueous entropy value and which is not extensively hydrated, produces only a very small ΔS when it is complexed.

Some ligands have more than one potential coordinating atom in their molecule so that chelate rings can be formed in their association with a metal ion. Such chelates are generally considerably more stable than the complexes involving unidentate ligands. The replacement of two unidentate ligands, A^{M-}, by a chelate, $(A-A)^{2m-}$ may be written,

$$MA_2(H_2O)_x^{(n-2m)} + (A-A)_{aq}^{2m-} \rightleftharpoons (H_2O)_x M \left\langle \begin{matrix} A \\ A \end{matrix} \right)^{(n-2m)} + 2A_{aq}^{m-} \text{ ---------- } (10)$$

This reaction will be expected to take place with an increase in entropy since there is an increase of one species in solution in going from left to right. It has been suggested by Schwarzenbach[27,28], that the greater stability of metal chelates compared with analogous unchelated complexes, named the "chelate effect" by him, is due to an entropy effect. These considerations do of course involve the assumption that there are no changes in hydration.

Williams[29] has pointed out, however, that the heats of formation cannot be ignored and that the chelate effect is, in part, an enthalpy effect. This can be seen especially in formation of complexes with uncharged ligands where the entropy change is not so large. The favourable enthalpy changes accompanying chelate formation for complexes of this type have been ascribed by Williams to a "built-in" effect. Once one donor atom of the ligand molecule is coordinated to the metal ion, the other donor atoms are held in place by the rest of the molecule. In forming a complex with a monodentate ligand, on the other hand, mutual repulsions of the polar groups must be overcome when bringing up the second ligand molecule so that this stage of the reaction will be more endothermic. Both enthalpy and entropy effects appear to contribute to the chelate effect, their relative importances depending upon the system being studied.

In general, it is best to supplement thermodynamic data with more direct data about the structure of the species which can sometimes be obtained by spectroscopic methods. In theory, it should be possible to devise a spectral technique which would enable every aspect of a molecular entity to be studied. Each technique has its limitations, however, and it is necessary to employ as many as possible if a reliable composite picture of the species under observation is to be established. A brief discussion of the principles involved in three of these techniques will be given in the next section.

Absorption of radiation in the infra-red region of the spectrum occurs due to changes in dipole moments in a molecule arising from bond stretching or bending. If no change in dipole moment takes place there will be no absorption. In many cases where absorption does occur as with C-H bonds these are often so numerous and their environments so similar that it becomes impossible to assign absorption bands to specific vibrations. The group occurring most frequently in complexes which best lends itself to investigation by I.R. spectroscopy is undoubtedly the C-O group. Being a functional group it is usually involved in bonding to the metal ion and many workers[30,31] have derived useful information about structure and bonding in complexes from changes in the I.R. spectrum of this group.

Raman spectroscopy can be considered to be supplementary to I.R. in that it is sensitive to symmetrical molecular vibrations during which there is no dipole moment change. The Raman effect[32] is a radiation scattering phenomenon, arising due to a change in polarisability within a molecule. The difference in frequency between the incident and scattered wave may correspond directly to the frequencies of vibration and rotation of the atoms within the molecule. Raman spectra reflect mainly covalent interactions between species in solution and Chantry and Plane[33] have studied the complex cyanides of some group Ib and group IIb metals using this technique.

N.M.R. is another technique which has recently been widely applied to structure determinations in solution[34,35]. A spinning proton acts as a small magnet which can be shown, from quantum mechanical considerations to have two possible orientations in a magnetic field. By suitable adjustment of magnetic and electromagnetic fields it is possible to induce protons to go from the low to the high energy state with a subsequent absorption of energy which can be detected. Protons in different environments absorb different amounts of energy and can therefore be distinguished. A change in environment of the protons on an organic ligand, for example, will occur on complex formation from which information about structure and bonding in the complex can be derived. Only non-labile protons are useful for studies of this type since, if a proton is continually changing its location only its average environment will be recorded. The protonation schemes of a number of complexes have been studied by Reilley[36] and Sawyer[37] by observing changes in chemical shifts of non-labile protons as the pH is varied.

In Part I of the present work, proton magnetic resonance studies have been made on N- methyliminodiacetic (N-MIDA) acid complexes. Protonation schemes have been established for the complexes formed between the acid and divalent magnesium, calcium, strontium and barium ions in aqueous solution and where possible binding sites have been elucidated.

In Part II, a cell incorporating glass and calomel electrodes has been used to determine the stability constants of the 1:1 and 1:2 alkaline earth metal complexes with N-MIDA. The stability constant for the magnesium monoglycinate complex has also been established using the above technique.

Part III is devoted to the calorimetric determination of the heats of formation of these complexes. The ligand is of interest since it represents one half of an ethylenediaminetetraacetic acid molecule and can thus be used directly in a discussion of the chelate effect.

PART I

Nuclear Magnetic Resonance Studies on Alkaline Earth N-MIDA Complexes

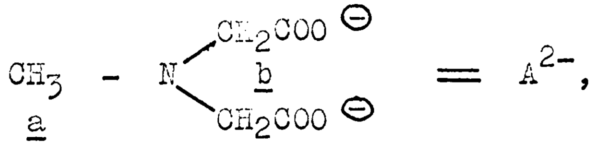
NUCLEAR MAGNETIC RESONANCE

Introduction

The conditions necessary to cause a proton to resonate are dependent upon its chemical environment. When exposed to a magnetic field the diamagnetic electrons surrounding the proton are induced to set up a small magnetic field which always opposes the main field. The effect of this is that a slightly larger applied field is required to bring the protons into resonance than would have been necessary in absence of the electrons. Consequently, protons surrounded by different electron densities will give proton magnetic resonance signals at different applied fields. Also, a change in the resonance position of any one proton will be observed if its electronic environment is disturbed.

The electron density surrounding a proton is dependent upon the electron affinities of the chemical groups in its vicinity. An electron attracting group like the carboxylate group will tend to decrease the electron density around a proton on a neighbouring carbon atom whereas the tendency of a group such as methyl to donate electrons will cause it to have the reverse effect; these effects result in a deshielding and shielding of the proton respectively. The deshielding of a proton results in it being brought into resonance at a slightly lower applied field. In contrast, a highly shielded proton will require a greater applied field since a larger opposing field, due to the greater density of electrons, has to be overcome before the resonance conditions for the proton can be established. These are short range effects which tend to influence, to an appreciable extent, only those groups attached to a carbon atom which is adjacent to the functional group. They may be transmitted further, however, if inductive groups such as oxygen or nitrogen atoms or double bonds are present in the molecule.

If the anion of N-MIDA is considered to be as shown in Figure I,



$$\underset{\underline{a}}{CH_3} - N \left< \begin{matrix} CH_2COO^{\ominus} \\ \underline{b} \\ CH_2COO^{\ominus} \end{matrix} \right. = A^{2-},$$

FIG. I

then due to free rotation of groups about single bonds the three methylene, a, protons and the four ethylene, b, protons will be equivalent but protons a will have a different environment from protons b. The b protons will be expected to absorb at the lower field strength of the two sets since they will be deshielded to a greater extent by the carboxylate groups. The anion has three functional groups, the nitrogen and the two carboxylates, which may be utilised in bonding. Complex formation would be expected to change the electron distribution around the protons causing a shift in their position of resonance. Bonding through the nitrogen should perturb a and b protons to the same extent but bond formation involving the carboxylate groups should only affect the b protons appreciably. Observed changes in the proton magnetic resonance of the non-labile protons in a ligand when it becomes complexed can yield much information about the nature of the coordination.

In a solution in which there exists an equilibrium between free ligand and complex, if the exchange of metal ions between ligands is rapid (>100 c.p.s.) then only one peak, representing the average of the two situations, will be observed for equivalent protons. If this exchange is slow, however, a broadening of the peak or two separate peaks will be seen representing the two proton environments. Useful kinetic data can be obtained from this effect. Day and Reilley[38] have determined qualitatively the labilities of individual metal-ligand bonds from the effects of the various possible symmetry states and their lifetimes on the N.M.R. spectra of the complexes. The longer lifetimes of the metal-nitrogen bonds with some ligands are shown to be due to steric effects which inhibit the entry of the incoming group necessary to replace the nitrogen.

If a strong complex is formed giving rise to large electronic perturbations, the chemical shift between the anion and the complex will be large and a stepwise variation in the position of the average peak will be observed as the ratio of complex to free anion changes. A study of the variation of the chemical shift with mole ratio for the lead (II) and bismuth (III) tartrate complexes has been made by Brannan and Sawyer[39]. A break in the graph at a lead (II) to tartrate ratio of 1:2 is considered to be indicative of two stable chelate species being formed.

From a study of the chemical shift differences between complexes and protonated species for a large number of metal-ethylenediaminetetra-acetic acid complexes Kula et al[37] were able to establish that the first two protons combine with the nitrogen atoms. From the variation of chemical shift with hydrogen ion concentration relative metal to ligand bond strengths were established and fairly satisfactory stability constants for the complexes were obtained.

In the present work, a proton magnetic resonance study of some alkaline earth complexes of N-MIDA has been made in an attempt to obtain information about the sites of bonding. Protonation schemes of the ligand have been established and relative bond strengths compared.

Preparation of Reagents

N-Methyliminodiacetic Acid: N-Methyliminodiacetic Acid, N-MIDA, was prepared following the method of Schwarzenbach et al[40]. The recrystallised product decomposed between 225 and 227°C. The following are the analysis figures for the acid.

$C_5H_9O_4N$	Theoretical	C,40.82	H,6.17	N,9.52%
(MW 147)	Found	C,40.62	H,5.91	N,9.63%

Potassium Hydroxide: Washed sticks of analar potassium hydroxide were dissolved in boiled out distilled water under an atmosphere of nitrogen. The carbon dioxide free solution was stored in the pyrex container of an automatic burette and was at all times protected from the atmosphere by soda-lime tubes. The solution was standardised by titrating against wieghed samples of potassium hydrogen phthalate until the results of duplicate experiments agreed within 0.1%.

Metal Chlorides: Stock solutions of analar magnesium, calcium, strontium and barium chlorides were prepared using carbondioxide free distilled water.

The magnesium and calcium solutions were analysed by means of an EDTA titration using Eriochrome Black T as indicator[41]. In the case of calcium the Mohr[I] procedure for chloride determination was also used.

Analysis of the strontium and barium solutions was achieved by a gravimetric technique[1] in which the metal ions were precipitated and weighed as their insoluble sulphates. All analyses agreed to within 0.2%.

<u>Buffer Solutions</u>: The buffer solutions used to standardise the glass electrodes were N.B.S. standard buffer solutions prepared according to Bates[42], using reagents of analar grade without further purification. They were potassium hydrogen phthalate, 0.05M, pH 4.008, potassium dihydrogen phosphate, 0.008695M plus disodium hydrogen phosphate, 0.03043M, pH 7.413, sodium borate, 0.01M, pH 9.180.

All water used had been distilled at least once and had been rendered carbondioxide free either by boiling or by bubbling out with nitrogen. Glassware was thoroughly cleaned before use with alcoholic potassium hydroxide followed by chromic acid and where possible steamed for thirty minutes. Where necessary, apparatus was dried using analar acetone which was evaporated off with dry filtered air. All volumetric apparatus was of grade"A" quality. Oertling and Mettler single-pan balances were used to weigh reagents.

Experimental

The N-methyliminodiacetic acid was converted to its potassium salt since sodium ion has been shown to complex to a certain extent with ligands of this nature[37]. It was necessary to use fairly concentrated solutions, greater than 0.2M, in order to obtain suitable N.M.R. signals.

A sealed capillary tube containing analar benzene was introduced in to the sample tube as an external reference standard. As a check, some experiments were run with an internal standard, 0.04 M tetramethylammonium bromide.

Solutions containing the anionic form of the acid were prepared and their pH was varied from about 12 to 0 by adding dropwise a 5N solution of hydrochloric acid. Approximately 0.5 milliliter samples were transferred to N.M.R. tubes after each addition of hydrochloric acid and their spectra recorded. For solutions in the high pH region, the pH of the bulk of the solution was taken while the spectrum was being run to take account of any variation due to carbon dioxide absorption.

In solutions containing metal ions, especially magnesium ion, care had to be taken to avoid metal hydroxide precipitation. The potassium hydroxide was added to the solution of metal chloride plus N-MIDA to achieve the highest pH attainable without precipitation.

Results

N.M.R. spectra for all the solutions have the general form shown in Figure 2. Peak (E) is due to the protons of the benzene reference while the three methylene and four ethylene protons of the N-MIDA are responsible for absorption peaks (A) and (B) respectively. The large absorption at (D) is due to water, the solvent.

A typical plot of the variation of chemical shift, δ(p.p.m. relative to benzene), with pH of the solutions for both a and b protons, is shown in Figure 3. In tables I to V are the results for the free anion and the Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} complexes of N-MIDA from which the above graphs were constructed.

The regions PQ and P'Q' of the S shaped curves in Figure 3 which were almost horizontal for the free anion and the magnesium and calcium complexes tended to show a decrease in δ with decreasing pH for the barium and strontium complexes. This decrease was attributed to some contribution to the position of the peak from the free anion, A^{2-}, and its mono-protonated form, HA^{-}.

The association constants for the complexes were known and in order to calculate values for these constants at the high ionic strengths used in the N.M.R. experiments the Davies equation was used to calculate an approximate activity coefficient. The concentrations of the ionic species were obtained by solving the quadratic equation (11);

$$[A^{2-}]^2\left\{K_1\left(1+\frac{[H^+]}{k_2}\right)\right\}+[A^{2-}]\left\{1+\frac{[H^+]}{k_2}-K_1(Tm-Ta)\right\}-Ta=0 \text{------}(11)$$

derived from the equations for the total acid,

$$Ta = [HA^-] + [A^{2-}] + [MA], \text{------------------------}(12)$$

total metal,

$$Tm = [M^{2+}] + [MA], \text{---------------------------}(13)$$

second dissociation constant of the acid,

$$k_2 = \frac{[H^+]\,[A^{2-}]}{[HA^-]}, \text{-------------------------------}(14)$$

and the association constant for the complex,

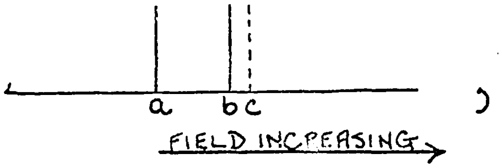
$$K_1 = \frac{[MA]}{[M^{2+}]\,[A^{2-}]}. \text{---------------------------------}(15)$$

In the cases of barium and strontium the absorption peak for the complex occurs at higher fields than either A^{2-} or HA^-, the mono-protonated anion. Since the recorded peak represents the average situation of the non-labile protons both A^{2-} and HA^- will tend to shift the peak downfield. The amount of this effect which is due to the HA^- can be calculated from equation (16),

$$x = \frac{[HA^-]}{Ta} \times 0.64, \text{--------------------------------}(16)$$

where x in p.p.m. is the small decrease in chemical shift and 0.64 p.p.m. is the total chemical shift (previously measured) arising from complete mono-protonation of the anion.

If x is now added to the actual chemical shift obtained the new value represents the weighted average of the proton environments in A^{2-} and MA. Schematically, the positions of the peaks can be considered to be;



where a is the A^{2-} peak, c represents the position of the complex peak and b is the obtained value corrected for HA^{-}. From the relationship,

$$\frac{b - a}{c - a} = \frac{[MA]}{Ta} \text{ ---------------------- } (17)$$

the absorption peak for the complex, c, can be determined. The results of this calculation are shown in table VI. In table VII chemical shift differences between the free anion and the complexes are compared for this system and for the two sets of corresponding protons of ethylenediaminetetra-acetic acid, EDTA, and di-(2-aminoethoxy)-ethanetetra-acetic acid, EGTA, c and d in Figure 4.

TABLE I

Variation of chemical shifts of Methylene (A) and

pH	11.93	11.49	11.12	10.91	10.73
B(p.p.m.)	3.37	3.37	3.37	3.37	3.34
A(p.p.m.)	4.20	4.20	4.20	4.20	4.18

pH	3.82	3.38	3.02	2.78	2.56
B(p.p.m.)	2.68	2.67	2.65	2.61	2.60
A(p.p.m.)	3.53	2.52	3.51	3.51	3.52

TABLE II

Variation of chemical shifts of Methylene (A) and magnesium

pH	9.76	9.20	8.62	8.36	8.14
B(p.p.m.)	3.22	3.23	3.21	3.21	3.16
A(p.p.m.)	4.01	4.01	3.99	3.98	3.94

pH	6.75	6.06	3.14	3.35	2.68
B(p.p.m.)	2.81	2.69	2.64	2.63	2.61
A(p.p.m.)	3.63	3.53	3.49	3.47	3.48

TABLE I

Ethylene (B) protons of N-MIDA anion with pH

10.45	10.24	10.08	9.76	9.52	8.96
3.30	3.25	3.21	3.13	2.92	2.79
4.12	4.07	4.04	3.95	3.75	3.60

2.36	1.92	1.53	1.20	0.95	0.78
2.52	2.47	2.36	2.29	2.26	2.23
3.46	3.48	3.43	3.40	3.40	3.38

TABLE II

Ethylene (B) protons of N-MIDA in its complex with pH

8.01	7.83	7.55	7.30	7.12	6.96
3.14	3.10	3.02	2.96	2.90	2.86
3.92	3.88	3.81	3.76	3.71	3.67

2.40	2.16	1.96	1.66	1.46	1.16	0.82	0.58
2.57	2.55	2.48	2.41	2.38	2.31	2.24	2.21
3.47	3.47	3.46	3.42	3.42	3.39	3.35	3.36

TABLE III

Variation of chemical shifts of Methylene (A) and Calcium

pH	9.66	8.95	8.00	6.86	6.61
B(p.p.m.)	3.25	3.24	3.22	3.13	3.01
A(p.p.m.)	4.14	4.13	4.09	3.99	3.88

pH	2.98	2.66	2.16	1.86	1.65
B(p.p.m.)	2.64	2.62	2.56	2.50	2.45
A(p.p.m.)	3.50	3.49	3.48	3.45	3.43

TABLE IV

Variation of chemical shifts of Methylene (A) and Strontiu

pH	9.96	9.52	9.22	9.00	8.79
B(p.p.m.)	3.42	3.34	3.32	3.29	3.26
A(p.p.m.)	4.26	4.23	4.16	4.12	4.08

pH	2.67	2.44	2.17	1.78	1.51
B(p.p.m.)	2.64	2.61	2.55	2.47	2.41
A(p.p.m.)	3.52	3.51	3.49	3.46	3.45

TABLE III

Ethylene (B) protons of N-MIDA in its complex with pH

6.53	6.42	6.32	6.20	6.02	5.82	4.09	1.48	1.21	0.88	0.65	0.29
2.96	2.93	2.89	2.85	2.79	2.73	2.63	2.43	2.38	2.28	2.25	2.19
3.82	3.79	3.74	3.69	3.63	3.58	3.51	3.43	3.41	3.38	3.36	3.34

TABLE IV

Ethylene (B) protons of N-MIDA in its complex with pH

8.55	8.29	7.99	7.72	7.43	6.30	3.41	1.23	1.03	0.82
3.17	3.09	2.98	2.90	2.84	2.72	2.70	2.37	2.30	2.29
3.99	3.93	3.82	3.73	3.66	3.55	3.55	3.44	3.42	3.40

TABLE V

Variation of chemical shifts of Methylene (A) and Barium

pH	10.20	9.96	9.71	9.52	9.46
B(p.p.m.)	3.41	3.39	3.35	3.34	3.31
A(p.p.m.)	4.27	4.24	4.21	4.19	4.17

pH	7.80	7.38	6.90	4.28	4.13
B(p.p.m.)	2.84	2.78	2.74	2.70	2.70
A(p.p.m.)	3.67	3.61	3.58	3.55	3.54

TABLE VI

Corrected Chemical Shifts for (A) protons of N-MIDA

Metal ion	$Tm.10^{1}$	$Ta.10^{1}$	pH	$K.10^{-2}$	$k.10^{10}$	$\left[A^{2-}\right].10^{2}$
Strontium	1.249	1.176	9.50	5.74	2.94	0.710
Barium	1.249	1.176	10.20	2.56	2.94	1.470

T A B L E V

Ethylene (B) protons of N-MIDA in its complex with pH

9.29	9.16	9.00	8.84	8.65	8.46	8.19
3.29	3.27	3.22	3.17	3.11	3.04	2.93
4.14	4.11	4.06	4.01	3.96	3.88	3.76
3.02	2.36	1.88	1.34	.88	.42	
2.66	2.60	2.50	2.36	2.28	2.23	
3.52	3.51	3.48	3.44	3.39	3.38	

T A B L E VI

in Barium and Strontium Complexes.

$[HA^-].10^2$	$[MA].10^1$	b(p.p.m.)	x(p.p.m.)	b+x(p.p.m.)	a(p.p.m.)	c(p.p.m.
1.023	1.003	4.22	.06	4.28	4.20	4.30
0.399	0.989	4.25	.02	4.27	4.20	4.28

TABLE VII

Chemical Shift Differences

	HA^-	MgA	CaA	SrA	BaA
	$(\delta_{A^{2-}} - \delta_{HA^-})$	$\Delta = (\delta_{A^{2-}} - \delta_{MA})$			
	MIDA				
a singlet	-0.64	-0.19	-0.06	+0.10	+0.08
b singlet	-0.64	-0.15	-0.12	+0.10	+0.10

	H_2A^{2-}	MgA^{2-}	CaA^{2-}	SrA^{2-}	BaA^{2-}
	$(\delta_{A^{4-}} - \delta_{H_2A^{2-}})$	$\Delta = (\delta_{A^{4-}} - \delta_{MA^{2-}})$			
	EDTA				
c singlet	-0.91	+0.01	+0.08	+0.16	+0.20
d singlet	-0.65	-0.03	-0.01	+0.04	+0.06
	EGTA				
c triplet	-0.69	-0.10	-0.03	+0.10	+0.16
d singlet	-0.62	-0.13	-0.05	+0.06	+0.08

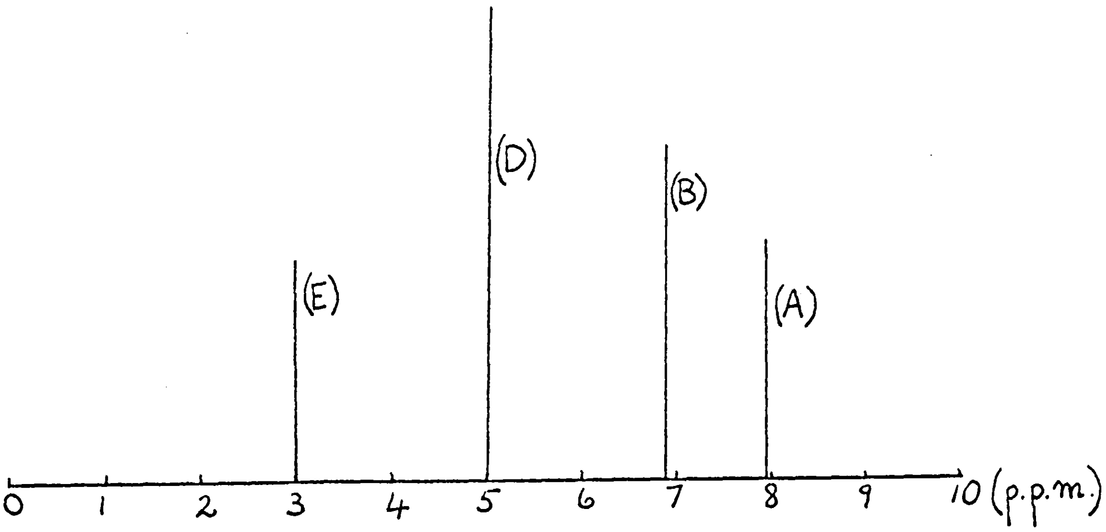


Fig. 2

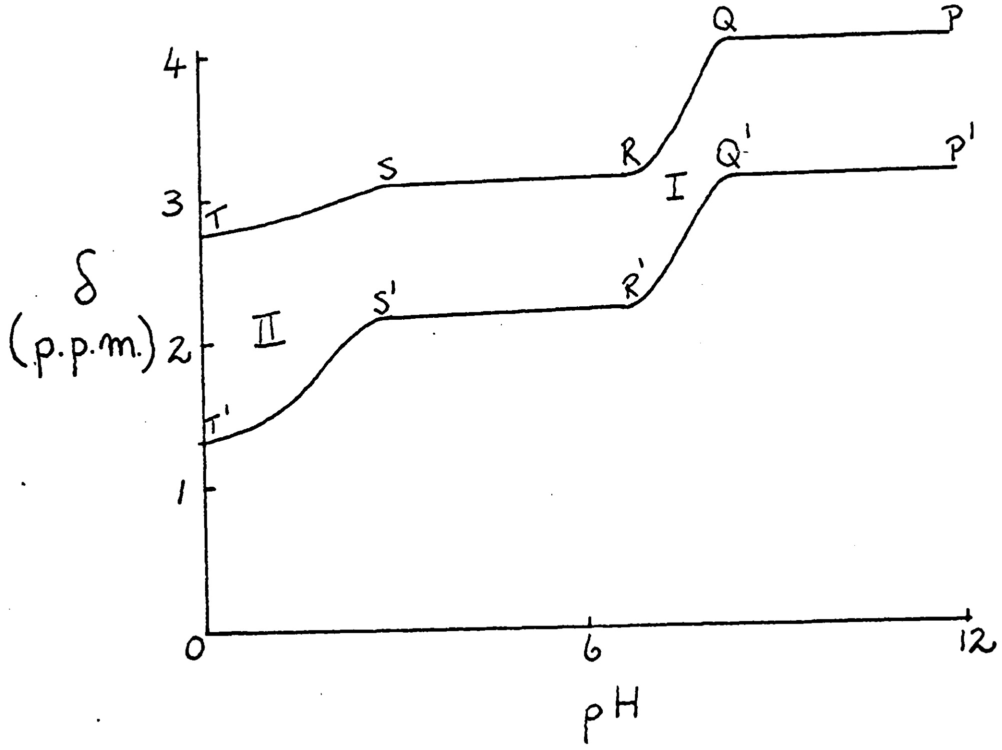
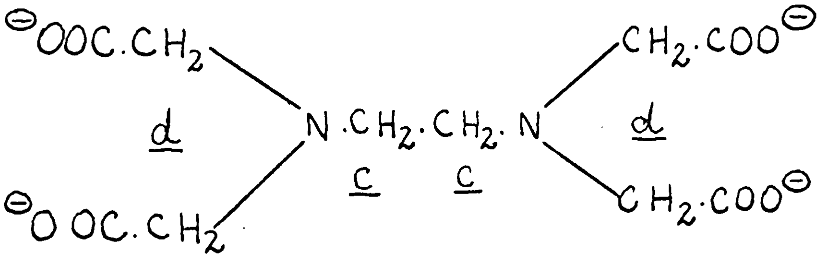
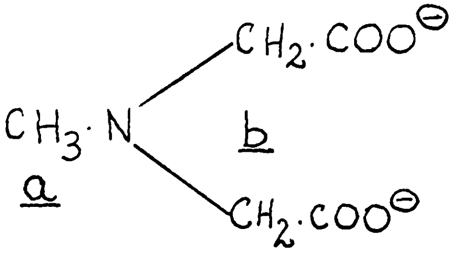


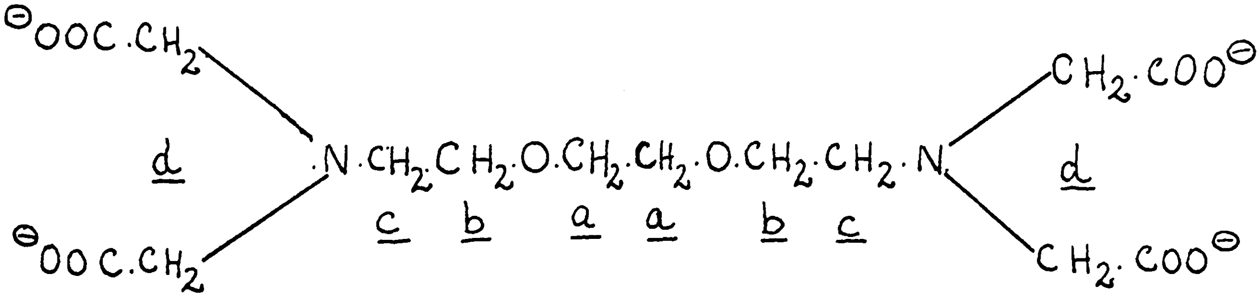
Fig. 3



$EDTA^{4-}$



$N-MIDA^{2-}$



$EGTA^{4-}$

Fig. 4

Discussion

For all alkaline earth complexes with the N-methyliminodiacetic acid anion, the nuclear magnetic resonance spectra showed two sharp singlets corresponding to the a and b protons. This is in contrast to the findings of Kula et al[37] for the alkaline earth complexes of the ethylenediamine tetra-acetate anion where the resonances for the Ca, Sr and Ba chelates all showed a broadening effect at intermediate pH regions. This was attributed to a slow exchange between metal ions and ligands at these hydrogen ion concentrations and the absence of any such broadening with N-MIDA complexes indicates that the metal ion-ligand exchange is rapid. Under these conditions only the average situation of the non-labile protons was recorded.

The variation in chemical shifts, δ, with pH for both the free anion of N-MIDA and the four complexes followed the general pattern shown in Figure 3. The plateau regions at intermediate pH values, RS and R'S' in Figure 3, are the chemical shifts of the a and b protons respectively of the monoprotonated ligand. Since the decrease in δ in going from the free anion (regions PQ and P'Q' in Figure 3) to the monoprotonated species is the same for both a and b hydrogens then this first proton must become attached to the nigrogen atom. The second protonation of the ligand occurs a much lower pH and since only the chemical shift of the b hydrogens is appreciably lowered, S'T' in Figure 3, this second proton is associated with the carboxylate groups. Rapid exchange of this proton between the two carboxylates must occur since no splitting or broadening of the b proton resonance is observed. Protonation schemes of this nature have been found for a number of aminocarboxylate ions which have previously been studied[36] and these have been confirmed by infra-red studies[43,44].

The pH range in which inflection I in Figure 3 occurs depends on the stability of the complex. More stable complexes requiring a greater concentration of hydrogen ions in the solution before appreciable protonation can occur. From inspection of the curves, the pH at which this inflection occurs for different metal ions is seen to follow the order of stability of the complexes. Variations in the position of inflection I are also observed when the metal ion concentration is varied. At high contrations of metal ions, however, the change in the position of the infection with metal ion concentration is small compared to the variation brought about by change of metal ion so that qualitative comparisons of stability are valid under these conditions. Inflection II in Figure 3 occurred at the same pH for all systems indicating that the metal ion was no longer associated with the ligand.

Sawyer and Tackett[44] have shown from infra-red studies of the carboxylate group for alkaline earth EDTA complexes that the spectra of these complexes under basic conditions are virtually identical with the spectrum of the EDTA anion suggesting predominantly ionic bonding for these groups. It has been suggested by Grigor'ev et al[45], however, that the shift to a higher value of the C-O stretching frequency in the Mg^{2+} ion complexes of iminodiacetic acid, IDA, and nitrilotriacetic acid, NTA, is indicative of covalent M-O bonding in these complexes. From variations in the absorption frequencies of C-H, C-N and N-H groups in the IDA complexes the above authors conclude that the covalency of the metal-nitrogen bond increases along the series $Ba < Sr < Ca < Mg$; the spectrum of the Ba complex being almost identical to that of the free anion.

There is little correlation of the values in table VII with factors such as charge-to-radius ratio of the metal ions. The non-labile protons, a and b on N-MIDA and c and d on EDTA and EGTA in Figure 4 are deshielded to a greater extent by Mg^{2+} than by Ca^{2+} which suggests stronger bonding in the magnesium complexes. The deshielding of the a protons indicates that nitrogen-metal bonds are formed in these complexes. The predominant inductive effect of the positively charged metal ion would be expected to produce deshielding of protons on the ligand but in many cases an increase in shielding is seen in table VII. It is clear that other factors must also influence the proton chemical shifts. One of these is "long-range" shielding caused by the electron distributions of neighbouring groups. This effect is the average of a number of different interactions and is highly dependent on the anisotropies of the distributions and on the various angles and distances involved. The magnitude of the effect will be sensitive to changes in the geometry of the complex and thus is different for different metal ions. The net chemical shifts are a combination of all these factors, so that in order for a systematic variation of chemical shifts with the electronegativities of different metal ions to exist, the inductive effect would have to outweight changes in the long range shielding. This has been shown to be the case for the Mg^{2+} and Ca^{2+} complexes but not for complexes with the Sr^{2+} and Ba^{2+} ions which have small inductive effects due to the low charge density on these large ions. In these complexes, inductive and long range shielding effects are of equivalent importance.

PART II

Association Constants for N-MIDA and Glycinate Complexes of the Alkaline Earth Metal Ions.

ASSOCIATION CONSTANTS

Introduction

A number of complexes of metal ions with the anions of aminopolycarboxylic acids have been characterised by the determination of stability constants by Schwarzenbach[46], Anderegg[47,48] and their co-workers at a constant ionic strength of 0.1. The determination of activity coefficients would be inexact for many of the highly charged ligand ions involved in these complexes and although the association constants are valid only at an ionic strength of 0.1, useful comparisons can be made with other constants obtained at the same ionic strength.

The method most used for the determination of association constants is the measurement of hydrogen ion activity by means of a glass electrode. A knowledge of the activity coefficient, f_{H^+}, of the hydrogen ion is necessary for the conversion of hydrogen ion activities to concentrations and at constant ionic strength, not greater than 0.1, it is possible to use the mean activity coefficients of hydrochloric acid at the appropriate concentration. Alternatively, the activity coefficients can be calculated using the modified form of the Debye - Huckel equation proposed by Davies[49],

$$-\log f_{H^+} = A z^2 \left(\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.3I\right), \text{---------}(18)$$

and this is the procedure adopted in the present work.

The dissociation constants for glycine and for the monoprotonated form of N-MIDA have been measured at 25°C. and an ionic strength of 0.1. Association constants for the divalent magnesium, calcium, strontium and barium mono- and di-N-methyliminodiacetate complexes and for the magnesium mono-glycinate complex have been obtained under the same conditions of temperature and ionic strength. An accurate knowledge of these association constants was necessary for the analysis of the enthalpy results to be described later.

Apparatus

E.m.f. measurements were made using the cell,

Ag/AgCl, HCl(0.2M)/ glass/ solution (I 0.1)/N/10 KCl,Hg_2Cl_2,Hg.

For experiments with N-MIDA a pair of glass electrodes of the screened type (E.I.L. type G.G.33.) were used and these were replaced by two Beckman General Purpose glass electrodes (Type 42, 41263) for the studies with glycine. With two independent glass electrodes in the cell, any irregularity in the behaviour of one of them was immediately detectable. These were used in conjunction with a calomel electrode and salt bridge of design shown in Figure (5). A small quantity (0.5 - 1ml) of triply distilled mercury was placed at the bottom of vessel (G) in Figure (5) and this was covered with a layer of calomel paste prepared by rubbing together in a mortar, calomel, mercury and a few drops of N/10 potassium chloride solution. The apparatus was then completely filled with N/10 potassium chloride solution from reservoir (D). Tube (F), having a platinum wire sealed through the tip, was placed in position as shown by means of a rubber bung (E), the joints being coated with paraffin wax to prevent stray potentials. The capillary tip (A) was bent to minimise the flow of solution from the salt bridge into the cell.

Titrations were made with an 'Agla' micrometer syringe which had a total capacity of 0.5 ml. and from which 2×10^{-4} ml. additions could be made with accuracy.

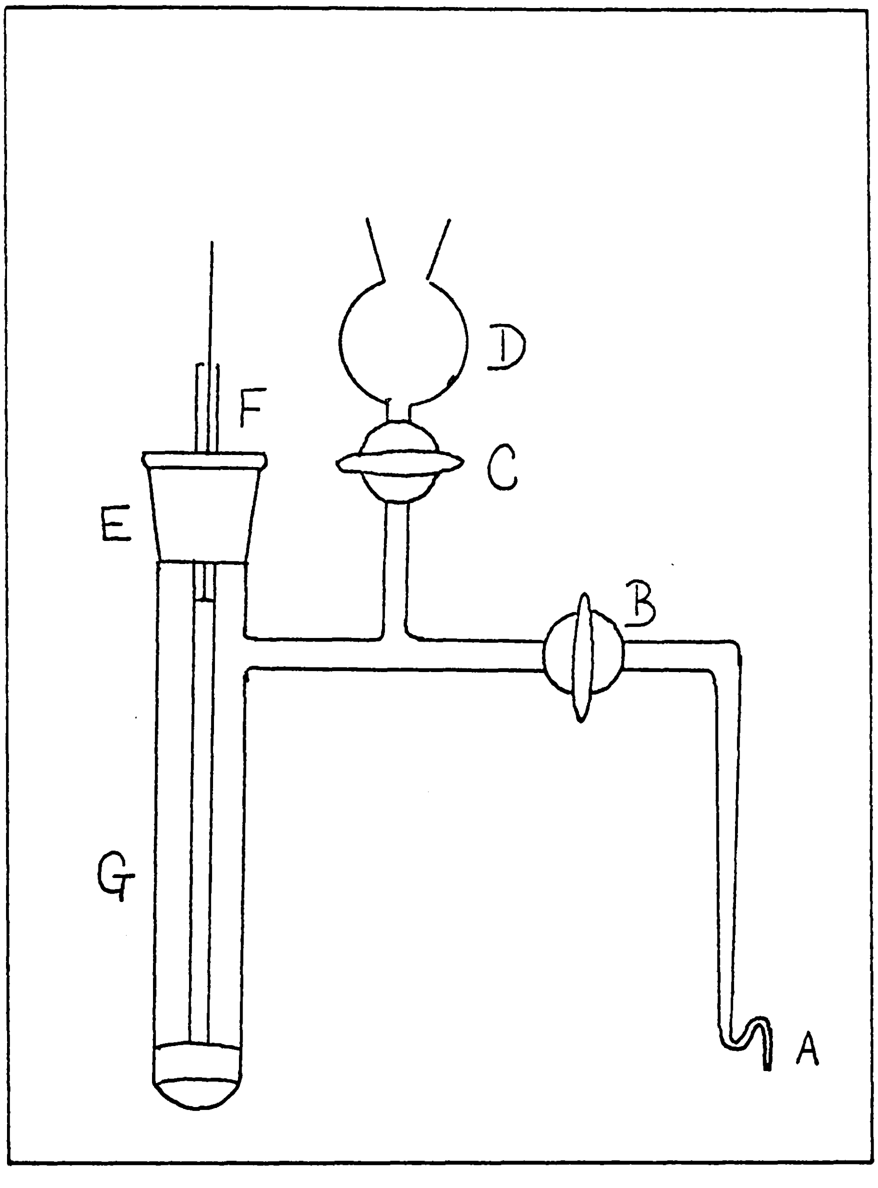


Fig. 5

Either a Pye potentiometer with a Vibron electrometer (E.I.L. model 33B) as null detector or a Beckman research pH meter were used to measure the e.m.f.s. All readings were reproducible to ± 0.1 m.v.

Experimental Technique

The cell is shown in Figure (6). A known volume of solution was introduced and the electrodes placed in the ground glass sockets. Nitrogen was bubbled through the capillary tube, A, to remove carbon dioxide and to stir the solution, and an outlet bubbler, B, prevented diffusion of air back into the cell. A capillary attachment from the micrometer syringe entered the cell by socket, C. When solution was initially put into the cell at least one hour was allowed for equilibration, but during a titration 10 to 15 minutes after each addition was all that was necessary.

In the determination of the dissociation constants of the acids, potassium hydroxide was added to a solution containing a known weight of the acid together with sufficient potassium chloride to establish an ionic strength of 0.1 at the mid-point of the buffer region. The results of measurements for which calculations showed that the ionic strength was not within 2% of the required value were discarded.

The complex formation experiments were made in two ways: (1) a solution containing the ligand, potassium hydroxide, and potassium chloride was titrated with the alkaline earth metal chloride solution, (2) the metal chloride, together with potassium chloride and ligand, was titrated with potassium hydroxide. In this way, a comprehensive range of both acid and metal concentrations

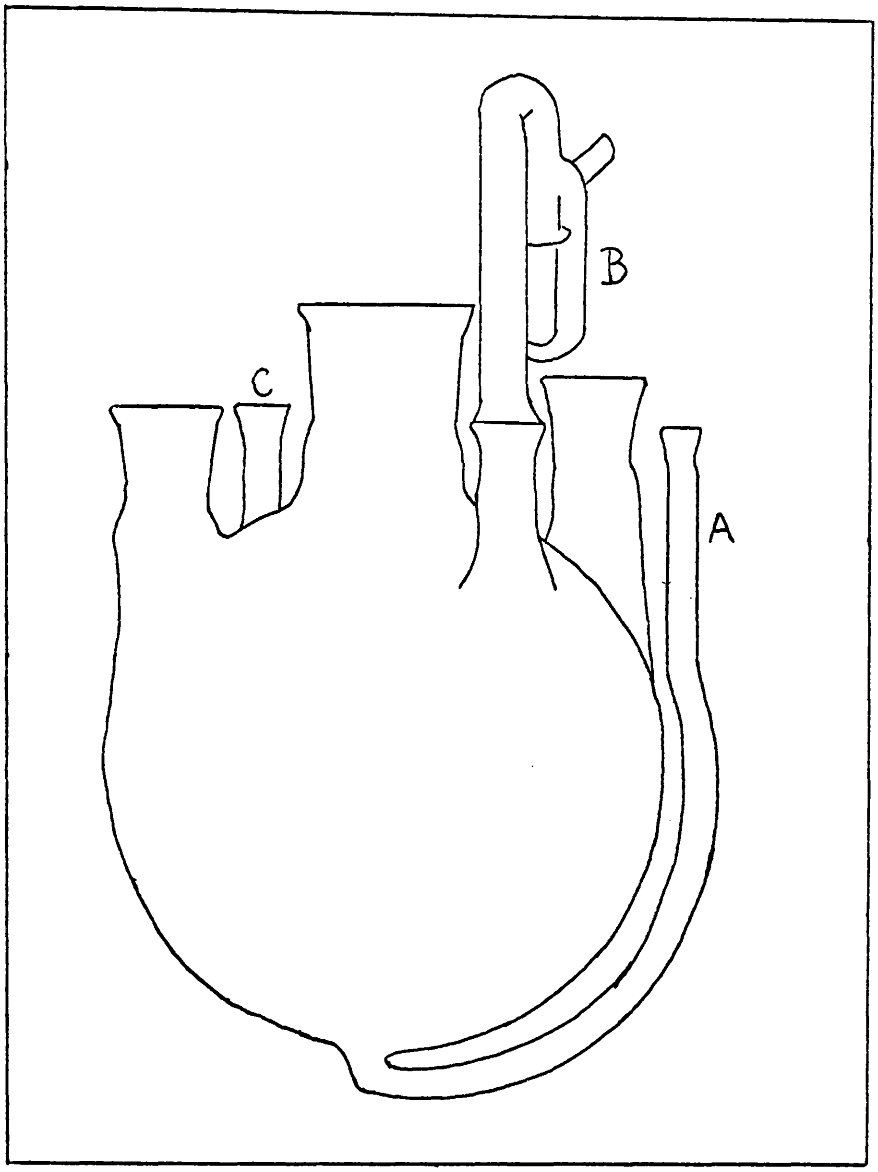


Fig. 6

could be covered.

The electrodes were standardised before and after each titration using N.B.S. standard buffer solutions prepared according to Bates[42]. Buffers were chosen with pH values within the range of those to be studied in the complex formation experiments.

Results

N-methyliminodiacetic acid, H_2A, dissociates in two steps,

$$H_2A \rightleftharpoons HA^- + H^+ \text{ ---------------------------(19)}$$

and $$HA^- \rightleftharpoons H^+ + A^{2-} \text{ ---------------------------(20)}$$

The titration curve is shown in Figure 7, and the first and second dissociation constants are sufficiently far apart for each equilibrium to be studied independently. Equilibrium 19 has been studied extensively by other workers, but it was necessary to obtain a reliable value for the second dissociation constant (reaction (20)) given by,

$$k_2 = \frac{[H^+]\,[A^{2-}]}{[HA^-]} \text{ -------------------------(21)}$$

In solutions containing the acid, potassium chloride and potassium hydroxide the concentrations of the ionic species were obtained from the equations for total acid,

$$Ta = [HA^-] + [A^{2-}] \text{ ----------------------------(22)}$$

and electroneutrality,

$$[H^+] + [K^+] = [HA^-] + 2[A^{2-}] + [OH^-] \text{ --------(23)}$$

Results of these calculations are shown in table (VIII). An exactly similar method was used for the titration of glycine, HG, and the results are given in table (IX).

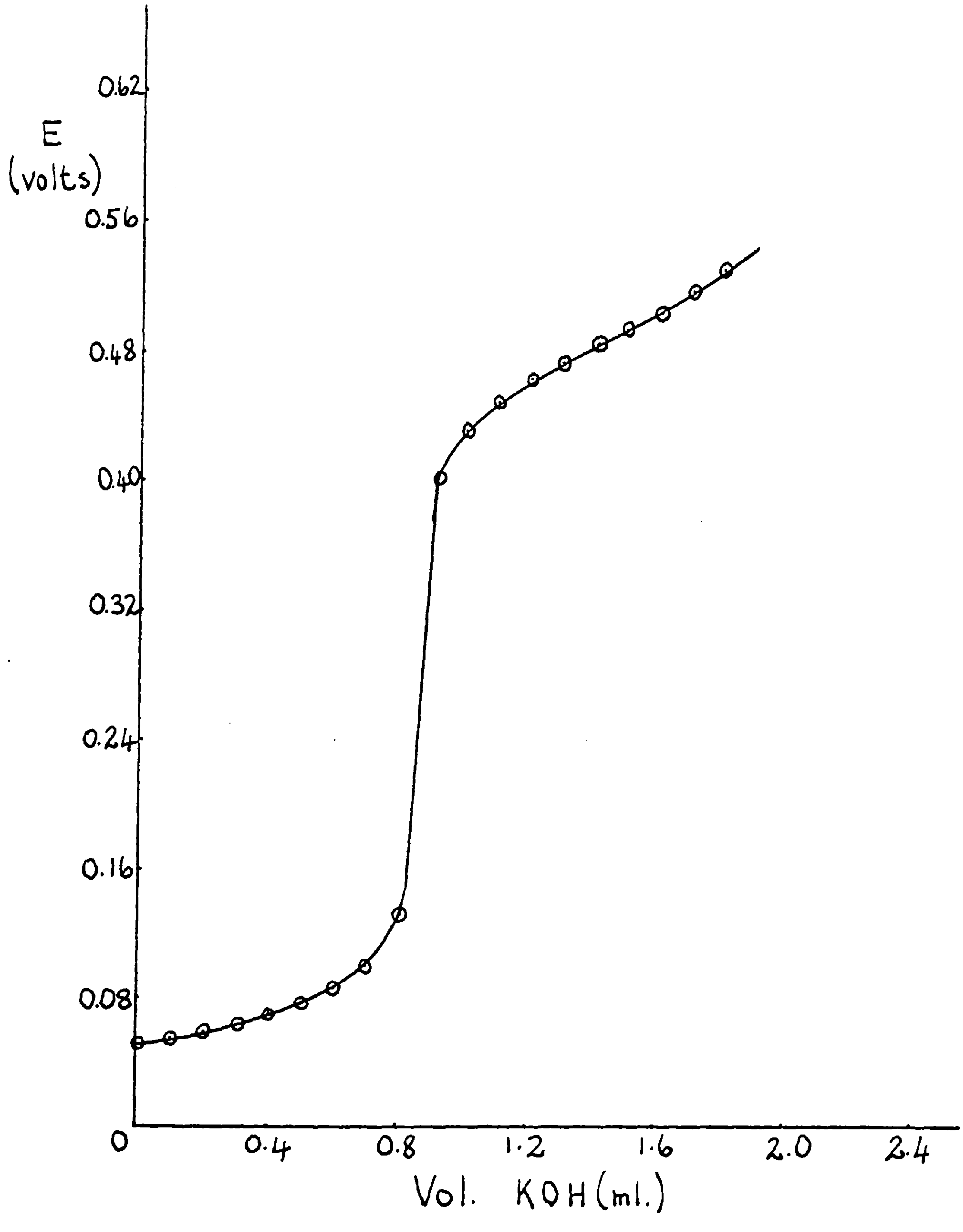

E
(volts)
0.62
0.56
0.48
0.40
0.32
0.24
0.16
0.08
0
0.4
0.8
1.2
1.6
2.0
2.4
Vol. KOH (ml.)

Fig. 7

The complex formation involving alkaline earth metal ions and N-methyliminodiacetate anion can be formulated in the following way,

$$M^{2+} + A^{2-} \rightleftharpoons MA \tag{24}$$

$$MA + A^{2-} \rightleftharpoons MA_2^{2-}. \tag{25}$$

The concentrations of ionic species in such solutions were obtained from the equations for total acid,

$$Ta = [HA^-] + [A^{2-}] + [MA] + 2[MA_2^{2-}], \tag{26}$$

total metal,

$$Tm = [M^{2+}] + [MA] + [MA_2^{2-}] \tag{27}$$

electroneutrality,

$$[K^+] + [H^+] + 2[M^{2+}] = [HA^-] + 2[A^{2-}] + 2[MA_2^{2-}] + [OH^-] + [Cl^-] \tag{28}$$

and the dissociation constant, k_2, for the acid.

From these equations, a graphical solution, similar to that of Gelles and Nancollas[50], was used in the determination of

$$K_1 = [MA] / [M^{2+}][A^{2-}] \tag{29}$$

and

$$K_2 = [MA_2^{2-}] / [MA][A^{2-}]. \tag{30}$$

The derived equation,

$$Y = XK_1 + K_1K_2 \tag{31}$$

where $X = \dfrac{\{Tm - Ta + [HA^-] + [A^{2-}]\}}{[A^{2-}]\{2Tm - Ta + [HA^-] + [A^{2-}]\}}$

and $Y = \dfrac{\{Ta - [HA^-] - [A^{2-}]\}}{[A^{2-}]^2\{2Tm - Ta + [HA^-] + [A^{2-}]\}}$

was solved graphically. Data for the alkaline earth complexes of N-MIDA are given in tables (X-XIV). Typical plots of X against Y are given in Figures (8-11), from which K_1 and K_2 were calculated from the slopes and intercepts of the lines respectively. The interpretation of these plots was such that the points at higher Y values were weighted more heavily in the determination of K_1 and points near the Y axis for which the concentration of the species MA_2^{2-} was larger were regarded as more important in the determination of K_2. An English Electric Leo computer model KDF9 was programmed for the determination of K_1 and K_2 by the method of least squares.

The small degree of association between the magnesium and glycinate ions resulted in a relatively high concentration of free magnesium ions in the solutions. The plots of X against Y for these experiments showed a distinct curvature in regions of high pH. This could be eliminated by making allowance for the presence of $MgOH^+$ ions in the solutions. The calculation involved the following steps.

From the equations for, total metal,

$$Tm = [M^{2+}] + [MG^+] + [MG_2] + [MOH^+] \text{ ---------------(32)}$$

total acid,

$$Ta = [MG^+] + 2[MG_2] + [HG] + [G^-] \text{ ---------------(33)}$$

electroneutrality,

$$2[M^{2+}] + [MG^+] + [H^+] + [K^+] + [MOH^+] = [G^-] + [OH^-] + [Cl^-] \text{ --(34)}$$

the dissociation constant for glycine,

$$k_2 = \frac{[H^+][G^-]}{[HG]}, \text{-----------------------------------}(35)$$

and the first and second association constants for the glycinate complexes,

$$K_1 = \frac{[MG^+]}{[M^{2+}][G^-]} \text{------}(36), \quad K_2 = \frac{[MG_2]}{[MG^+][G^-]} \text{------}(37)$$

the equation

$$Y^1 = X^1K_1 + K_1K_2 \text{--------------------}(38)$$

was derived in which,

$$Y^1 = \frac{\{Ta - [HG] - [G^-] + [MgOH^+]\}}{[G^-]^2\{2Tm - Ta + [HG] + [G^-] - 2[MOH^+]\}}$$

and

$$X^1 = \frac{\{Tm - Ta + [HG] + [G^-] - 2[MOH^+]\}}{[G^-]\{2Tm - Ta + [HG] + [G^-] - 2[MOH^+]\}}$$

The concentration of HG, from which $[G^-]$ could be calculated (35), was obtained from the equation,

$$[HG] = Ta + [OH^-] - [K^+] - [H^+] + [MOH^+] \text{----------------}(39)$$

in which $[MOH^+]$ is the only unknown. It was necessary, therefore, to use a reiterative proceedure by assuming as a first approximation the absence of MOH^+. An approximate value of K_1 was obtained from which the concentration of M^{2+} could be calculated, and hence the concentration of MOH^+ from,

$$K_h = \frac{[MOH^+]}{[M^{2+}][OH^-]}, \text{---}(40)$$

The approximate value of MOH^+ was then used in order to obtain a better approximation.

Results of this calculation are given in table (XV) and Figure (12) is a typical plot of X^1 against Y^1 showing the first approximation and the corrected line. Since within experimental error this line passed through the origin it was assumed that the concentration of MA_2 was too small to be significant.

TABLE VIII

k_2 Determination for N-MIDA

Run 1.

$Ta.10^3$	$[K^+].10^3$	$-\log[H^+]$	$[HA^-].10^3$	$[A^{2-}].10^3$	$k_2.10^{10}$
4.297	6.000	9.483	2.631	1.665	2.67
4.299	5.575	9.296	3.048	1.251	2.66
4.295	6.341	9.619	2.302	1.993	2.67
4.294	6.511	9.682	2.139	2.155	2.68
4.294	6.596	9.715	2.058	2.236	2.68
4.293	6.681	9.746	1.977	2.317	2.70
4.293	6.766	9.777	1.896	2.397	2.71
4.292	6.851	9.809	1.816	2.476	2.71

Run 2.

$Ta.10^3$	$[K^+].10^3$	$-\log[H^+]$	$[HA^-].10^3$	$[A^{2-}].10^3$	$k_2.10^{10}$
5.853	9.284	9.696	2.504	3.349	2.69
5.860	8.285	9.411	3.477	2.383	2.66
5.858	8.603	9.505	3.166	2.692	2.66
5.857	8.830	9.533	2.944	2.913	2.69
5.855	9.057	9.636	2.723	3.132	2.67
5.857	8.717	9.568	3.053	2.804	2.69
5.853	9.398	9.726	2.395	3.458	2.71
5.856	8.944	9.599	2.833	3.023	2.69

$$\text{Mean } k_2 = 2.68\ (\pm .01).10^{-10}$$

TABLE IX

k_2 Determination for Glycine

Run 1.

$Ta.10^3$	$[K^+].10^3$	pH	$[HG].10^3$	$[G^-].10^3$	$k_2.10^{10}$
15.285	6.593	9.379	10.231	5.054	2.64
15.254	7.402	9.479	9.397	5.857	2.65
15.223	8.208	9.572	8.566	6.657	2.66
15.193	9.011	9.666	7.741	7.452	2.65
15.163	9.810	9.759	6.923	8.240	2.65
15.132	10.607	9.854	6.110	9.022	2.64

Run 2.

$Ta.10^3$	$[K^+].10^3$	pH	$[HG].10^3$	$[G^-].10^3$	$k_2.10^{10}$
9.630	4.913	9.694	4.780	4.850	2.63
9.615	5.519	9.803	4.177	5.438	2.62
9.644	4.306	9.586	5.387	4.257	2.63
9.659	3.696	9.474	6.001	3.658	2.62
9.601	6.123	9.915	3.584	6.017	2.61
9.586	6.725	10.032	3.000	6.586	2.61

Mean $k_2 = 2.63(\pm .02).10^{-10}$

TABLE X

Magnesium N-Methyliminodiacetate, K_1 and K_2

Run 1.

Ta.10^3	Tm.10^3	$[K^+].10^3$	pH
5.330	2.918	8.611	9.287
5.327	3.565	8.607	9.164
5.325	3.888	8.605	9.111
5.324	4.211	8.602	9.057
5.323	4.534	8.600	9.012
5.320	5.017	8.597	8.946
5.319	5.340	8.594	8.900
5.317	5.823	8.591	8.839

Run 2.

5.206	4.211	9.176	9.440
5.205	4.534	9.173	9.391
5.204	4.856	9.171	9.345
5.202	5.179	9.168	9.293
5.201	5.501	9.166	9.251
5.198	6.145	9.161	9.168
5.195	6.788	9.156	9.098
5.193	7.430	9.151	9.039

$[MA] \cdot 10^3$	$[MA_2^{2-}] \cdot 10^4$	$Y \cdot 10^{-6}$	$X \cdot 10^{-2}$
1.929	2.437	0.999	1.745
2.217	2.063	1.465	3.290
2.341	1.823	1.717	4.184
2.434	1.687	2.025	5.176
2.532	1.444	2.298	6.185
2.640	1.222	2.786	7.839
2.671	1.266	3.234	9.123
2.719	1.247	3.886	11.087

Mean $K_1 = 3.08 \times 10^3$ and $K_2 = 1.52 \times 10^2$

2.781	2.107	1.142	2.638
2.917	1.834	1.328	3.306
3.032	1.605	1.535	4.033
3.098	1.624	1.832	4.879
3.176	1.489	2.097	5.740
3.279	1.396	2.727	7.664
3.363	1.273	3.381	9.713
3.448	1.055	3.996	11.775

Mean $K_1 = 3.14 \times 10^3$ and $K_2 = 1.19 \times 10^2$

TABLE X

Run 3.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
5.485	4.695	9.745	9.486
5.483	5.017	9.743	9.434
5.482	5.340	9.740	9.388
5.480	5.662	9.738	9.341
5.479	5.984	9.735	9.299
5.477	6.466	9.731	9.239
5.474	7.109	9.726	9.170
5.471	7.751	9.721	9.099

Run 4.

4.532	3.242	8.035	9.601
4.530	3.888	8.031	9.494
4.527	4.534	8.027	9.388
4.525	5.179	8.022	9.296
4.523	5.823	8.018	9.216
4.521	6.145	8.016	9.177
4.520	6.466	8.014	9.145
4.518	7.109	8.010	9.083

$[MA].10^3$	$[MA_2^{2-}].10^5$	$Y.10^{-6}$	$X.10^{-2}$
3.294	5.966	0.872	2.650
3.396	5.705	1.050	3.228
3.495	4.597	1.232	3.856
3.568	4.409	1.448	4.558
3.642	3.452	1.659	5.290
3.718	3.150	2.028	6.500
3.814	1.806	2.522	8.191
3.828	4.082	3.191	10.196

Mean $K_1 = 2.99 \times 10^3$ and $K_2 = 2.8 \times 10^1$

2.255	14.772	0.797	1.948
2.553	10.610	1.136	3.216
2.743	9.196	1.624	4.830
2.882	7.715	2.184	6.713
2.985	6.433	2.798	8.792
3.007	7.020	3.184	9.972
3.054	5.810	3.479	11.049
3.107	5.290	4.190	13.414

Mean $K_1 = 2.99 \times 10^3$ and $K_2 = 8.0 \times 10^1$

T A B L E X

Run 5.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
1.666	2.433	2.987	9.400
1.664	3.565	2.984	9.225
1.663	4.211	2.982	9.143
1.662	4.856	2.981	9.075
1.662	5.179	2.980	9.046
1.661	5.823	2.978	8.992
1.660	6.466	2.977	8.941
1.659	7.109	2.975	8.894
1.658	8.072	2.973	8.831

Run 6.

2.053	6.467	3.171	8.504
2.052	6.788	3.171	8.485
2.052	7.110	3.170	8.465
2.051	7.431	3.169	8.448
2.050	7.752	3.168	8.430
2.050	8.073	3.167	8.410
2.049	8.393	3.166	8.387

$[MA].10^3$	$[MA_2^{2-}].10^5$	$Y.10^{-7}$	$X.10^{-3}$
0.986	5.290	0.739	1.797
1.114	2.798	1.187	3.124
1.145	2.538	1.490	3.959
1.171	2.128	1.785	4.791
1.184	1.839	1.926	5.201
1.204	1.364	2.209	6.025
1.214	1.313	2.523	6.891
1.218	1.510	2.862	7.794
1.220	1.807	3.382	9.165

Mean $K_1 = 3.50 \times 10^3$ and $K_2 = 3.03 \times 10^2$

0.971	4.047	2.257	7.275
0.982	3.617	2.347	7.643
0.991	3.312	2.447	8.026
1.001	2.924	2.535	8.390
1.009	2.640	2.633	8.768
1.007	2.858	2.785	9.234
0.999	3.367	2.975	9.762

Mean $K_1 = 2.84 \times 10^3$ and $K_2 = 3.20 \times 10^2$

TABLE X

Run 7.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.015	9.956	2.813	8.022
2.015	9.955	2.860	8.066
2.015	9.955	2.906	8.106
2.014	9.954	2.953	8.147
2.014	9.953	3.000	8.188
2.014	9.953	3.046	8.230
2.014	9.952	3.093	8.268
2.014	9.951	3.140	8.309
2.014	9.951	3.186	8.351

$[MA] . 10^4$	$[MA_2^{2-}] . 10^5$	$Y . 10^{-7}$	$X . 10^{-4}$
7.164	2.682	5.598	1.790
7.587	2.817	5.245	1.678
7.959	3.214	4.996	1.588
8.335	3.591	4.763	1.506
8.728	3.871	4.527	1.427
9.140	4.058	4.292	1.353
9.457	4.732	4.165	1.298
9.818	5.175	4.004	1.241
10.206	5.479	3.831	1.185

Mean $K_1 = 2.92 \times 10^3$ and $K_2 = 12.7 \times 10^2$

Average K_1 from runs 1, 2, 3, 4, and 7 $= 3.02(\pm 0.07) . 10^3$

Average K_2 from runs 1, 2, 5 and 6 $= 2.25(\pm 0.87) . 10^2$

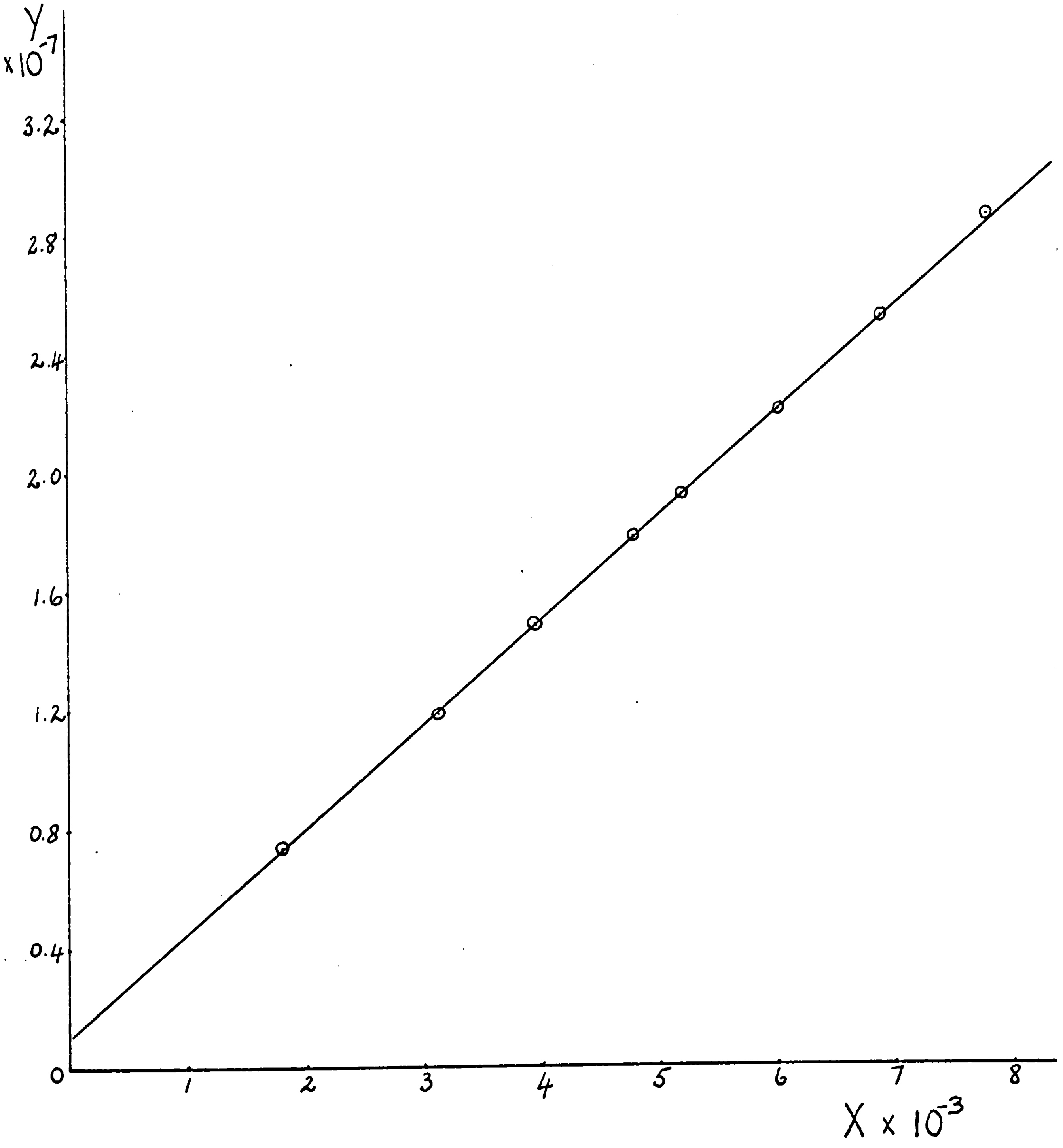


Fig. 8

TABLE XI

Calcium N-Methyliminodiacetate, K_1 and K_2

Run 1.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
1.547	2.075	2.411	8.733
1.546	2.488	2.409	8.644
1.545	2.901	2.408	8.554
1.544	3.314	2.407	8.491
1.544	3.726	2.405	8.426
1.543	4.138	2.404	8.367

Run 2.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
1.748	5.166	2.973	8.577
1.743	7.213	2.965	8.409
1.741	8.232	2.961	8.348
1.740	8.639	2.959	8.326
1.739	9.351	2.957	8.287
1.736	10.567	2.952	8.230

$[MA].10^4$	$[MA_2^{2-}].10^6$	$Y.10^{-7}$	$X.10^{-3}$
7.503	14.194	3.781	4.918
7.890	2.569	4.712	6.380
7.938	6.423	6.071	8.130
8.155	0.000	7.058	9.656
8.162	1.998	8.427	11.438
8.113	6.870	9.952	13.329

Mean $K_1 = 6.96 \times 10^3$ and $K_2 = 4.89 \times 10^2$

$[MA].10^3$	$[MA_2^{2-}].10^5$	$Y.10^{-8}$	$X.10^{-4}$
1.127	2.556	0.737	1.042
1.145	2.226	1.130	1.614
1.160	1.629	1.304	1.884
1.163	1.492	1.377	1.995
1.165	1.455	1.514	2.195
1.170	1.254	1.740	2.532

Mean $K_1 = 6.76 \times 10^3$ and $K_2 = 4.78 \times 10^2$

T A B L E XI

Run 3.

Ta.10^3	Tm.10^3	$[K^+].10^3$	pH
2.733	9.930	3.839	7.673
2.733	9.929	3.885	7.705
2.733	9.928	3.932	7.738
2.733	9.927	4.025	7.802
2.732	9.926	4.118	7.865
2.732	9.925	4.211	7.928
2.732	9.923	4.304	7.990
2.731	9.922	4.397	8.053

Run 4.

2.541	8.029	3.820	7.990
2.540	8.334	3.818	7.971
2.539	8.639	3.817	7.955
2.538	8.944	3.815	7.939
2.537	9.249	3.814	7.921

$[MA].10^3$	$[MA_2^{2-}].10^5$	$Y.10^{-8}$	$X.10^{-4}$
1.059	1.495	2.246	2.931
1.100	1.703	2.150	2.798
1.147	1.659	2.042	2.662
1.234	1.931	1.874	2.437
1.321	2.161	1.725	2.239
1.407	2.424	1.596	2.068
1.485	3.097	1.499	1.927
1.564	3.746	1.410	1.801

Mean $K_1 = 7.44 \times 10^3$ and $K_2 = 9.68 \times 10^2$.

1.196	2.800	1.772	1.267
1.195	2.899	1.860	1.333
1.201	2.638	1.936	1.381
1.204	2.469	2.015	1.432
1.202	2.618	2.106	1.500

Mean $K_1 = 6.94 \times 10^3$ and $K_2 = 5.91 \times 10^2$.

TABLE XI

Run 5.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.522	9.261	3.781	7.955
2.521	9.464	3.780	7.943
2.520	9.667	3.779	7.931
2.520	9.870	3.778	7.920
2.519	10.073	3.777	7.907
2.518	10.276	3.776	7.898
2.518	10.479	3.775	7.886

$[MA].10^3$	$Y.10^{-8}$	$X.10^{-4}$
1.397	1.253	1.945
1.393	1.296	2.004
1.388	1.341	2.065
1.385	1.383	2.124
1.376	1.439	2.193
1.379	1.469	2.242
1.372	1.522	2.309

Mean $K_1 = 7.32 \times 10^3$

Average K_1 from runs 1, 2, 3, 4, 5 $= 7.08(\pm.23).10^3$

Average K_2 from runs 1, 2, 4 $= 5.19(\pm.50).10^2$

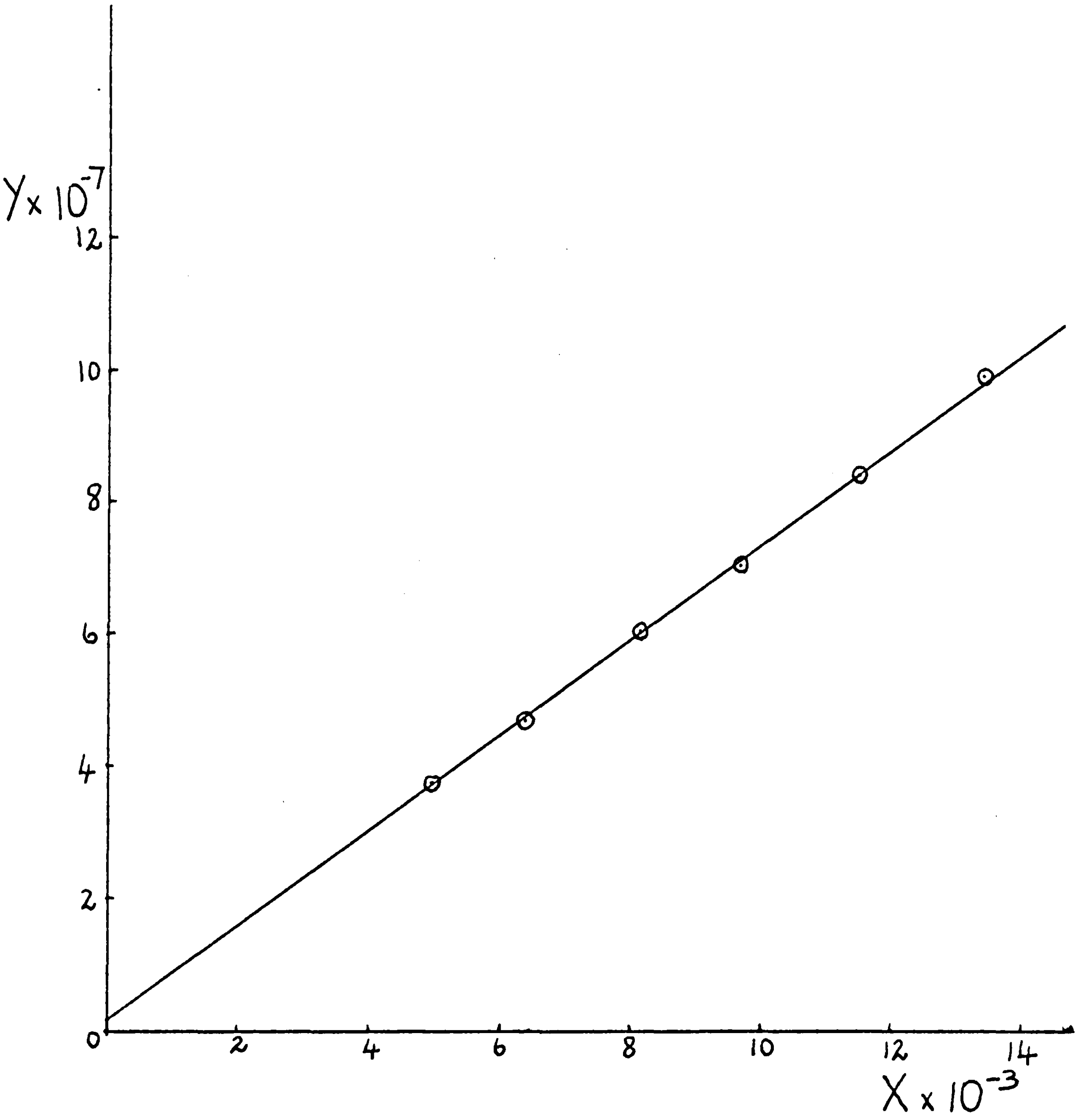


Fig. 9

TABLE XII

Strontium N-Methyliminodiacetate, K_1 and K_2.

Run 1.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.334	8.447	3.504	8.769
2.333	8.796	3.503	8.751
2.332	9.146	3.502	8.737
2.332	9.495	3.501	8.720
2.331	9.844	3.500	8.705
2.331	10.193	3.499	8.692
2.329	10.890	3.498	8.662
2.329	11.238	3.497	8.649

Run 2.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.338	9.864	3.277	8.531
2.338	9.863	3.370	8.605
2.338	9.863	3.417	8.641
2.338	9.862	3.463	8.678
2.337	9.861	3.510	8.715
2.337	9.861	3.556	8.750
2.337	9.860	3.603	8.783

$[MA].10^3$	$[MA_2^{2-}].10^6$	$Y.10^{-6}$	$X.10^{-3}$
1.007	6.193	3.093	3.248
1.011	7.071	3.237	3.393
1.020	4.448	3.336	3.517
1.021	6.662	3.499	3.672
1.028	5.265	3.613	3.803
1.034	4.067	3.729	3.935
1.040	5.309	4.014	4.225
1.043	5.170	4.146	4.365

Mean $K_1 = 9.40 \times 10^2$ and $K_2 = 4.25 \times 10^1$.

$[MA].10^3$	$[MA_2^{2-}].10^5$	$Y.10^{-6}$	$X.10^{-3}$
0.821	0.663	4.423	4.783
0.901	0.782	3.981	4.300
0.939	0.928	3.803	4.097
0.980	0.902	3.613	3.897
1.022	0.831	3.433	3.711
1.059	1.047	3.303	3.558
1.093	1.404	3.198	3.423

Mean $K_1 = 9.10 \times 10^2$ and $K_2 = 7.47 \times 10^1$

T A B L E XII

Run 3.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.816	9.889	4.021	8.587
2.816	9.888	4.114	8.652
2.815	9.887	4.161	8.685
2.815	9.886	4.207	8.716
2.815	9.886	4.254	8.745
2.815	9.885	4.300	8.777
2.814	9.884	4.393	8.837
2.814	9.881	4.579	8.958

Run 4.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.610	9.893	3.742	8.606
2.609	9.892	3.835	8.671
2.609	9.891	3.882	8.702
2.609	9.890	3.928	8.736
2.609	9.890	3.975	8.770
2.609	9.889	4.021	8.802
2.608	9.887	4.124	8.872

$[MA^-] \cdot 10^3$	$Y \cdot 10^{-6}$	$X \cdot 10^{-3}$
1.078	3.347	3.606
1.168	3.017	3.279
1.215	2.860	3.128
1.258	2.741	3.001
1.297	2.642	2.889
1.340	2.533	2.775
1.421	2.358	2.580
1.570	2.094	2.267

Mean $K_1 = 9.04 \times 10^2$ and $K_2 = 2.88 \times 10^1$.

$[MA] \cdot 10^3$	$[MA_2{}^{2-}] \cdot 10^6$	$Y \cdot 10^{-6}$	$X \cdot 10^{-3}$
0.989	6.633	3.397	3.777
1.067	8.006	3.108	3.450
1.102	11.361	3.008	3.319
1.146	9.073	2.856	3.167
1.188	8.130	2.730	3.034
1.225	9.878	2.635	2.921
1.306	14.289	2.450	2.699

Mean $K_1 = 8.86 \times 10^2$ and $K_2 = 5.42 \times 10^1$

TABLE XII

Run 5.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.620	8.791	3.932	8.775
2.620	9.140	3.931	8.759
2.619	9.489	3.930	8.744
2.618	9.838	3.929	8.729
2.618	10.186	3.927	8.714

$[MA].10^3$	$[MA_2^{2-}].10^5$	$Y.10^{-6}$	$X.10^{-3}$
1.109	1.508	2.565	2.831
1.117	1.447	2.666	2.946
1.123	1.419	2.769	3.063
1.129	1.346	2.869	3.178
1.134	1.345	2.975	3.296

Mean $K_1 = 8.82 \times 10^2$ and $K_2 = 8.05 \times 10^1$.

Average K_1 from runs 1, 2, 3, 4, 5 $= 9.04\ (\pm.16).10^2$

Average K_2 from runs 1, 2, 4, 5 $= 6.30\ (\pm1.4).10^1$

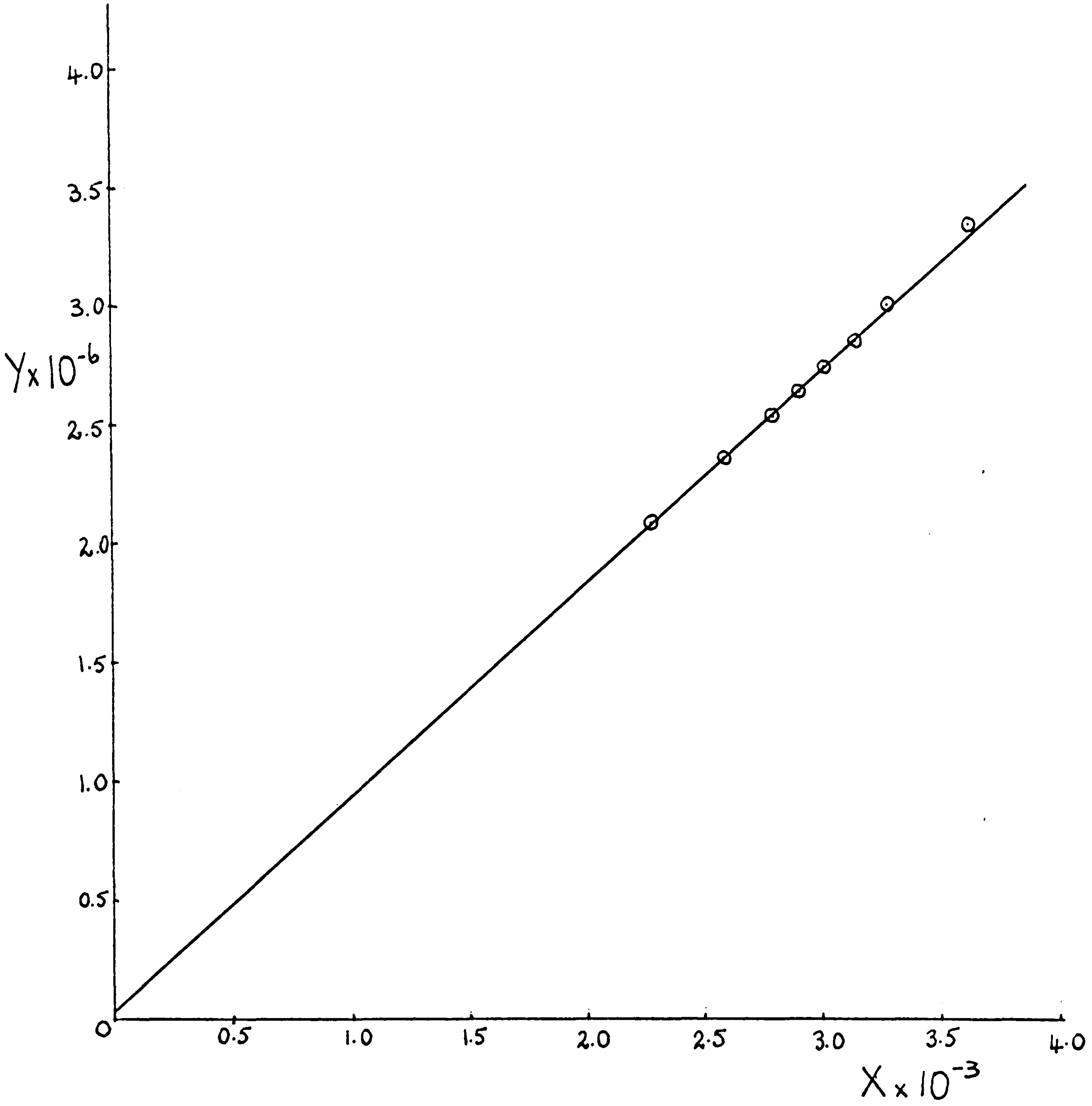


Fig. 10

TABLE XIII

Barium N-Methyliminodiacetate, K_1 and K_2

Run 1.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
3.107	8.456	4.667	9.024
3.107	8.651	4.666	9.017
3.105	9.041	4.664	9.003
3.104	9.430	4.662	8.989
3.103	9.819	4.660	8.974

Run 2.

2.752	9.806	3.733	8.714
2.751	9.805	3.826	8.782
2.751	9.803	3.919	8.843
2.751	9.802	4.012	8.902
2.750	9.801	4.104	8.964
2.750	9.799	4.197	9.021
2.750	9.798	4.290	9.078
2.749	9.797	4.382	9.138
2.749	9.796	4.475	9.199
2.749	9.794	4.568	9.261

$[MA].10^3$	$[MA_2^{2-}].10^5$	$Y.10^{-5}$	$X.10^{-3}$
1.153	2.381	6.390	1.336
1.161	2.289	6.506	1.363
1.182	1.766	6.665	1.410
1.196	1.576	6.892	1.463
1.210	1.417	7.124	1.517

Mean $K_1 = 3.98 \times 10^2$ and $K_2 = 2.69 \times 10^2$

0.739	2.160	11.184	2.487
0.811	2.104	9.997	2.237
0.876	2.519	9.199	2.046
0.938	3.137	8.575	1.889
1.007	3.187	7.857	1.737
1.065	3.973	7.425	1.623
1.124	4.712	7.020	1.520
1.183	5.316	6.625	1.425
1.244	5.847	6.254	1.339
1.301	6.561	5.949	1.265

Mean $K_1 = 4.16 \times 10^2$ and $K_2 = 1.68 \times 10^2$

TABLE XIII

Run 3.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
2.674	9.802	4.012	8.972
2.674	9.801	4.058	9.001
2.674	9.801	4.104	9.031
2.674	9.799	4.197	9.090
2.673	9.798	4.290	9.152

Run 4.

2.503	8.662	3.803	9.057
2.501	9.441	3.800	9.029
2.500	9.701	3.799	9.019
2.499	9.961	3.798	9.009
2.499	10.220	3.797	9.002
2.497	10.738	3.794	8.984

$[MA].10^4$	$[MA_2^{2-}].10^5$	$Y.10^{-5}$	$X.10^{-3}$
9.055	7.763	8.161	1.781
9.311	8.345	7.948	1.721
9.593	8.751	7.693	1.661
10.127	9.734	7.269	1.555
10.684	10.536	6.843	1.456

Mean $K_1 = 4.13 \times 10^2$ and $K_2 = 1.96 \times 10^2$

8.806	5.708	7.205	1.615
9.038	5.495	7.682	1.736
9.111	5.413	7.836	1.775
9.156	5.499	8.044	1.820
9.259	5.189	8.125	1.853
9.356	5.232	8.498	1.939

Mean $K_1 = 3.91 \times 10^2$ and $K_2 = 2.28 \times 10^2$.

Average K_1 from runs 1, 2, 3, 4 = $4.05(\pm .10).10^2$

Average K_2 from runs 1, 2, 3, 4 = $2.15(\pm .33).10^2$

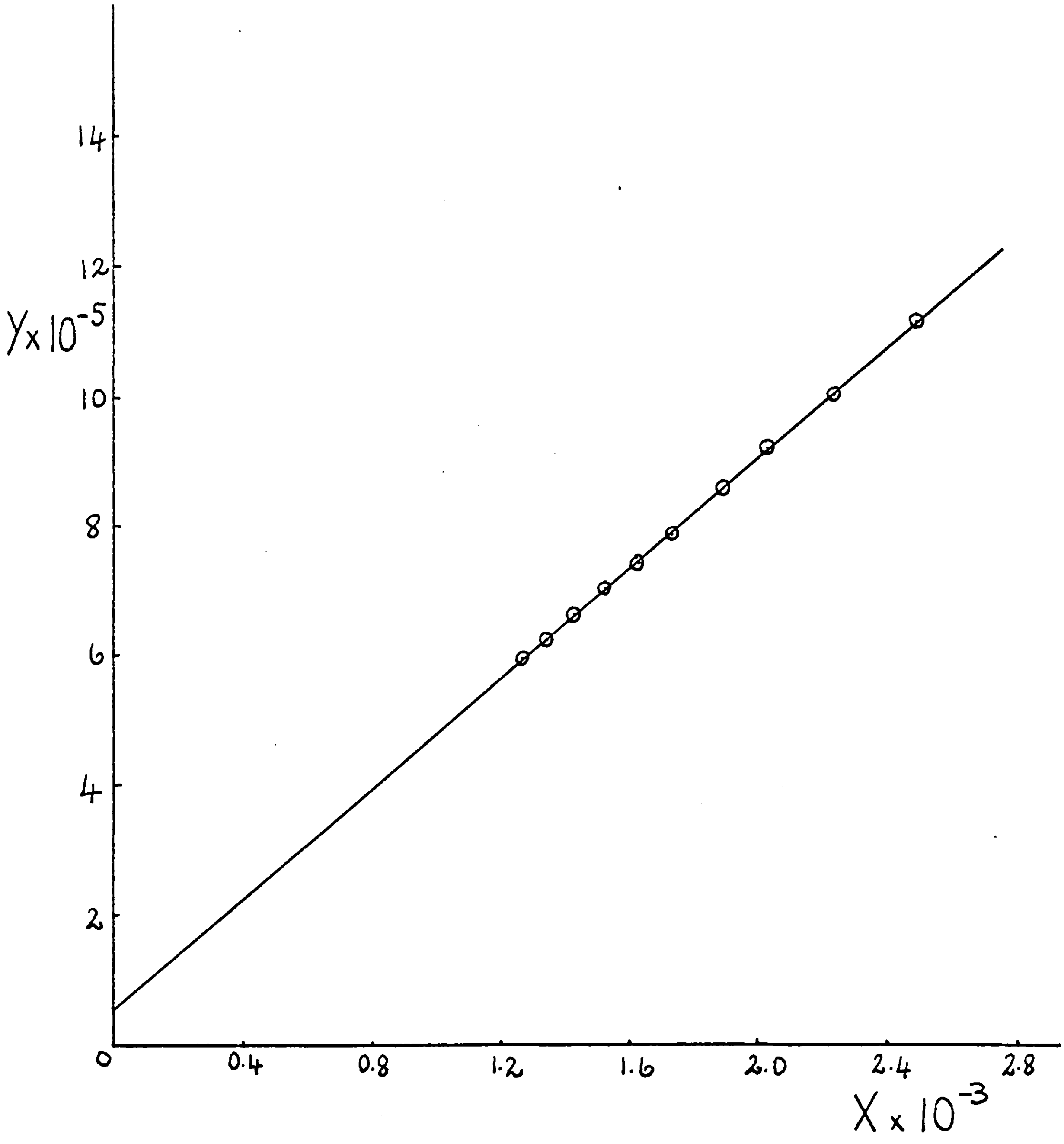


Fig. 11

TABLE XIV

K_1 and K_2 Values for Alkaline Earth-N-Methyliminodiacetate complexes at 25°C. and Ionic Strength, 0.1.

	Mg	Ca	Sr	Ba
K_1	3.02×10^3	7.08×10^3	9.04×10^2	4.05×10^2
K_2	2.25×10^2	5.19×10^2	6.30×10^1	2.15×10^2

TABLE XV

Determination of K_1 for Magnesium Glycinate

Run 1.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
9.698	3.312	4.308	9.550
9.707	3.315	3.902	9.475
9.717	3.319	3.495	9.400
9.727	3.322	2.881	9.275

Run 2.

$Ta.10^3$	$Tm.10^3$	$[K^+].10^3$	pH
15.157	5.090	5.739	9.431
15.142	5.085	6.143	9.480
15.127	5.080	6.545	9.528

$[MG^+] . 10^4$	$[MOH^+] . 10^5$	$X . 10^{-2}$	$Y . 10^{-3}$
2.528	1.970	1.196	2.840
2.304	1.670	1.328	3.254
2.099	1.400	1.487	3.406
1.751	1.100	1.818	4.248

Mean $K_1 = 2.26 \times 10^1$

$[MG^+] . 10^4$	$[MOH^+] . 10^5$	$X . 10^{-2}$	$Y . 10^{-3}$
5.068	2.30	0.905	1.684
5.381	2.50	0.843	1.570
5.692	2.80	0.788	1.456

Mean $K_1 = 1.90 \times 10^1$

T A B L E XV

Run 3.

$T_a.10^3$	$T_m.10^3$	$[K^+].10^3$	pH
10.256	10.237	2.473	9.090
10.240	10.221	3.087	9.221
10.230	10.211	3.495	9.297
10.220	10.201	3.902	9.371
10.210	10.190	4.308	9.443
10.194	10.175	4.916	9.543
10.164	10.145	6.127	9.742

$[MG^+].10^4$	$[MOH^+].10^5$	$X.10^{-2}$	$Y.10^{-3}$
4.074	2.20	2.464(2.47)	6.130(6.24)
5.000	2.90	1.966(1.98)	5.031(5.15)
6.289	3.51	1.740(1.75)	4.589(4.79)
6.170	4.10	1.546(1.56)	4.109(4.27)
6.719	4.80	1.397(1.41)	3.802(3.98)
7.474	5.90	1.223(1.24)	3.513(3.74)
8.860	9.10	0.973(0.99)	3.010(3.40)

(Brackets include X and Y data before correction for MOH^+.)

Mean $K_1 = 2.07 \times 10^1$.

Average K_1 from runs 1, 2, 3 $= 2.08(\pm 0.16).10^1$

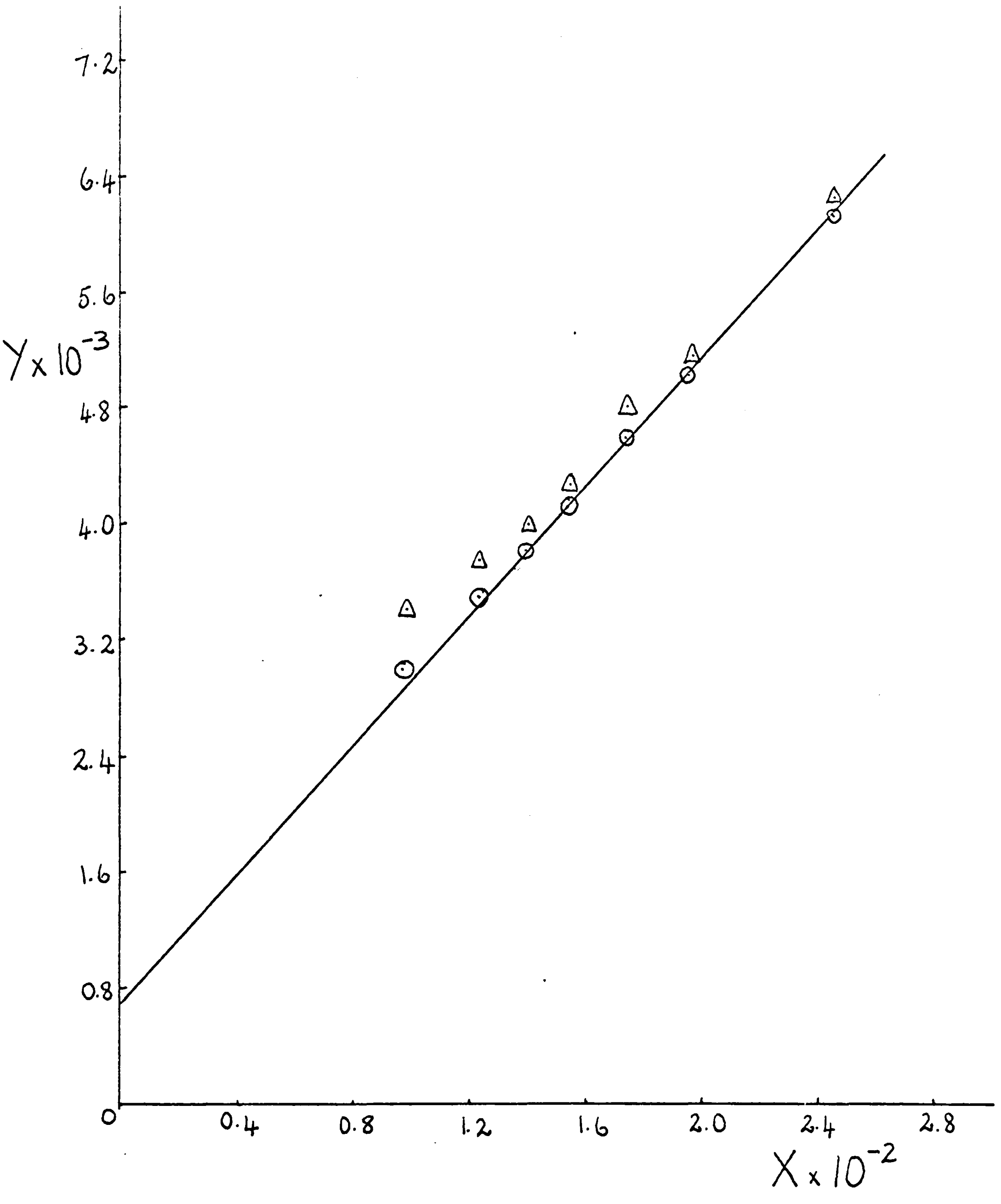


Fig. 12

Discussion

The alkaline earth metal cations were designated "Class A" metal ions according to the classification of Schwarzenbach[51]. In this group are included the cations for which purely electrostatic bonding predominates. The association constants of complexes formed with these metal ions will be expected to increase with decreasing cationic size. However, since the radii of the hydrated ions, r_h, may decrease for a particular series as the crystallographic radius, $r_{cryst.}$, increases, the trends in K for a given series of cations may be in different directions with different ligands. Irregularities will be expected depending on the extent of hydration of the complex or ion-pair[52]. Values of $K_{ass.}$ for the alkaline earth metal ion complexes[53] of the weakly associating iodates, intrates, sulphates and thiosulphates increase as r_h increases but with strongly associating ligands such as, oxalate, malonate, glycinate and aspartate, $K_{ass.}$ increases as $r_{cryst.}$ increases. In the case of the inorganic oxy-acid ligands, the measured values are undoubtedly related to the radii of the hydrated and not the bare cations whereas with the organic ligands the coulombic forces of association are strong enough for them to co-ordinate directly with the cation.

It is seen in the present work that the association constants do not follow the electrostatic potential of the cation for N-MIDA. This trend is also found with other multidentate aminopolycarboxylate ions. It is not possible to decide whether this behaviour can be attributed to differences in hydration without considering the additional thermodynamic properties. To this end, ΔH and ΔS values for the formation of the alkaline earth complexes of N-MIDA and glycine have been obtained in the following section.

PART III

Calorimetric Heats of Formation of Alkaline Earth-N-MIDA and Glycinate Complexes

CALORIMETRY

Introduction

The great interest in the aminocarboxylate ions lies in their ability to form very stable complexes with a wide variety of metal ions. This has resulted in their frequent use as analytical reagents for the determination of metal ions in solution. Much of the work, stimulated by the application of the ligand-field theory, has been done with the transition metal complexes, particularly with the EDTA molecule, whereas the alkaline earth cations have received less attention. The latter form a particularly suitable series for study and, if the bonding were purely electrostatic, the order of stability would be expected to follow the inverse order of ionic radii. It has been shown in the previous section that this is often not the case, the stability of the magnesium complex being anomalously low for a number of aminopolycarboxylate ligands. To gain a greater insight into factors affecting the equilibrium it is necessary to obtain heat and entropy data for the formation of these complexes in solution.

Many attempts have been made to calculate ΔH form the variation in equilibrium constants with temperature. The variation can be described by an equation of the form,

$$\log K = a + bT + cT^2 \ldots\ldots,$$

in which the parameters a, b and c can be obtained by substituting values of K at three temperatures and solving three simultaneous equations. Values of ΔH can then be calculated by differentiating log K with respect to temperature and while these values can be reliable if a large enough temperature range is covered the accuracy obtained by this method is frequently very poor[54,55]. There are, therefore, obvious advantages in measuring the heats of complex formation by a direct calorimetric method.

A number of calorimeters have been developed for the measurement of heats of solution and heats of complex formation. Most of them are of the constant environment type, the temperature of which is controlled such that a measured thermodynamic property can be assigned to this temperature.

A calorimeter, whose design has become the standard for many subsequent instruments was developed by Pitzer[56] for sensitive measurements at low concentrations of reactants. This calorimeter had a copper resistance thermometer ($\sim 100\,\Omega$) incorporated as one arm of a D.C. Wheatstone bridge. The calorimeter was kept at constant temperature in a water bath. The internal heating element consisted of insulated copper wire protected by a thin silver sheath. An electronic timer was used to record the duration of the heating currents to 1/200 of a second. Mixing was effected by breaking a glass phial on the blade of a rotary stirrer, and temperature changes of 3×10^{-4} °C. could be detected. A calorimeter of similar design has been used in recent work by Staveley[57] in which the mixing device was a glass bottle with ground glass stoppers top and bottom. Both stoppers could be released at the same time. A temperature sensitivity of 5×10^{-5}°C. was reported for this calorimeter.

Lange and Robinson[58] in 1931 studied heats of dilution with a system of twin adiabetic calorimeters in an attempt to eliminate external disturbances. Two symmetrically constructed calorimeter vessels were placed under similar conditions in a thermally homogeneous medium, whereby any remaining thermal disturbances between outside and inside were duplicated in both vessels. The small heat effects accompanying the reaction were then produced in one of the calorimeters and the temperature differences before and after the reaction were measured as accurately as possible. Each calorimeter contained a section of a 1,500 juntion thermopile and the heat change was derived from the change of e.m.f. with time.

More recently automatic recording of temperature changes have been introduced and caloimetric work has been reported by Cobble[59] and Izatt[60] in which the output from a D.C. Wheatstone bridge was aplified and fed to a chart recorder. Thermistors have been developed which are very stable and have a large temperature coefficient of resistance and these have been incorporated into a number of calorimeters[60,61].

In the present work, a pair of twin adiabatic calorimeters are described in which thermistors were employed as the sensing elements. Using these calorimeters, heats of formation of alkaline earth N-methyliminodiacetates and glycinates have been determined.

Apparatus:

The differential thermistor calorimeters are shown in Figure 13 and Plate I. They consisted of two silvered Dewar flasks, A, of 500 ml. capacity, cemented into brass containers, B. The rubber O-rings, C, between the tops of these containers and the screwed-down lids, D, ensured a water-tight seal. To achieve efficient thermal insulation, a solid cylindrical teflon bung, E, 4 cm. in length, was cemented to the underside of each lid. Four holes in the lid of each Dewar accommodated a platinum wire heater, of known resistance, F, a vibro-stirrer diaphragm, G, a thermistor, H, and a mixing device, I. In order to reduce to a minimum any heating effects caused by unequal stirring, both stirring rods were driven from the same vibrorotatory motor, (Vibro-Mischer, Messrs. Shandon and Co. Ltd., England) by means of a specially designed chuck, J. The brass containers were bolted together and were completely immersed in a thermostat at 25±.01°C.

The heater design is shown in Figure 14. It consisted of a hollow pyrex glass tube, A, 1 cm. in diameter and 6 cm. in length attached to a similar tube, B, 0.7 cm. in diameter and 12 cm. in length. The wider tube was closed at the bottom end except for a small hole, C, through which the platinum heating wire, D, (42 s.w.g.) was led. The wire was then wound round this tube and passed through another small hole, C, near the junction of the tubes. At both holes, enamelled copper lead wires, E, were attached to the platinum, sealed in the holes and led out of the calorimeter through the narrow tube. The heating wire was insulated by painting with a

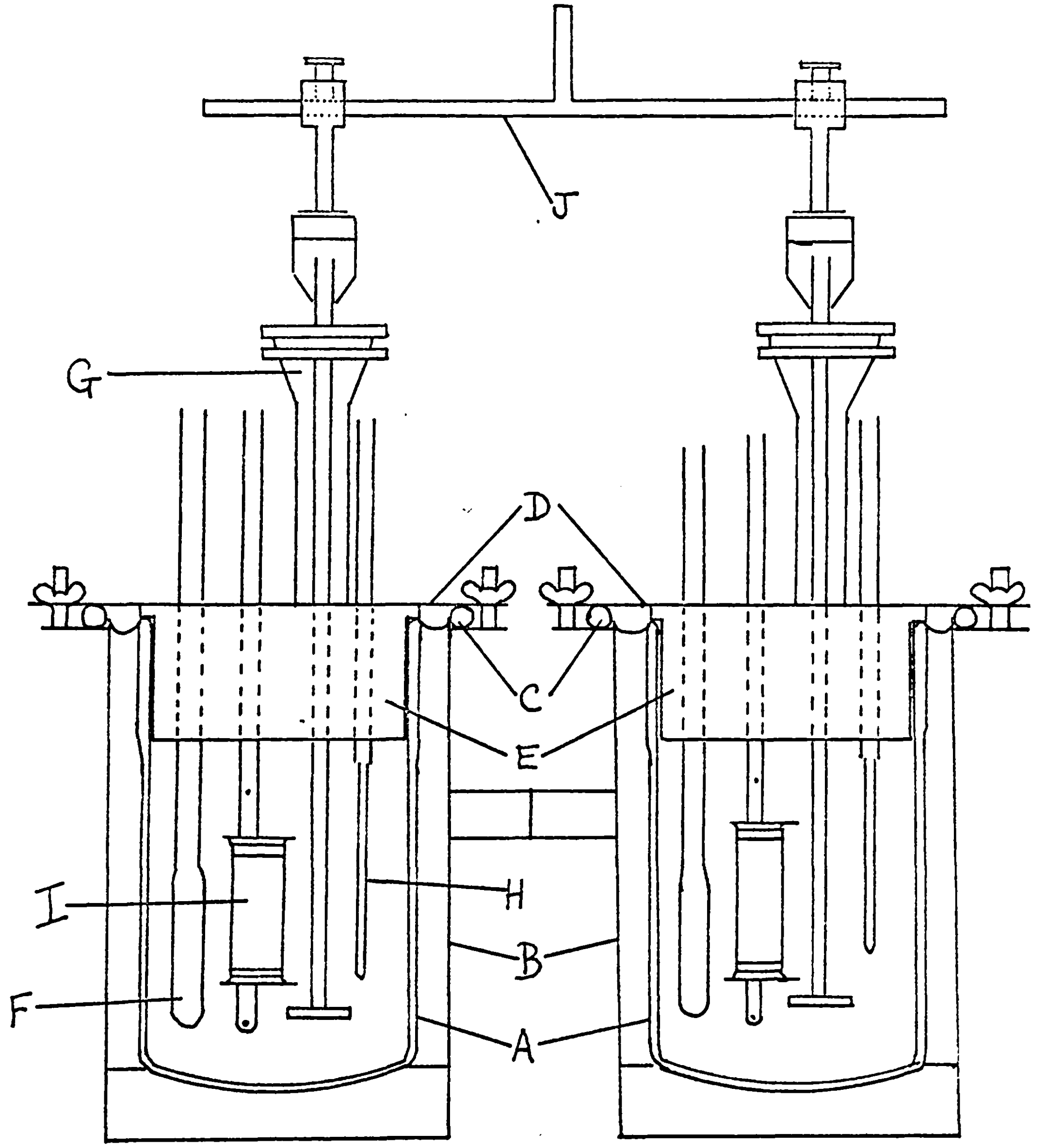


Fig. 13

PLATE I

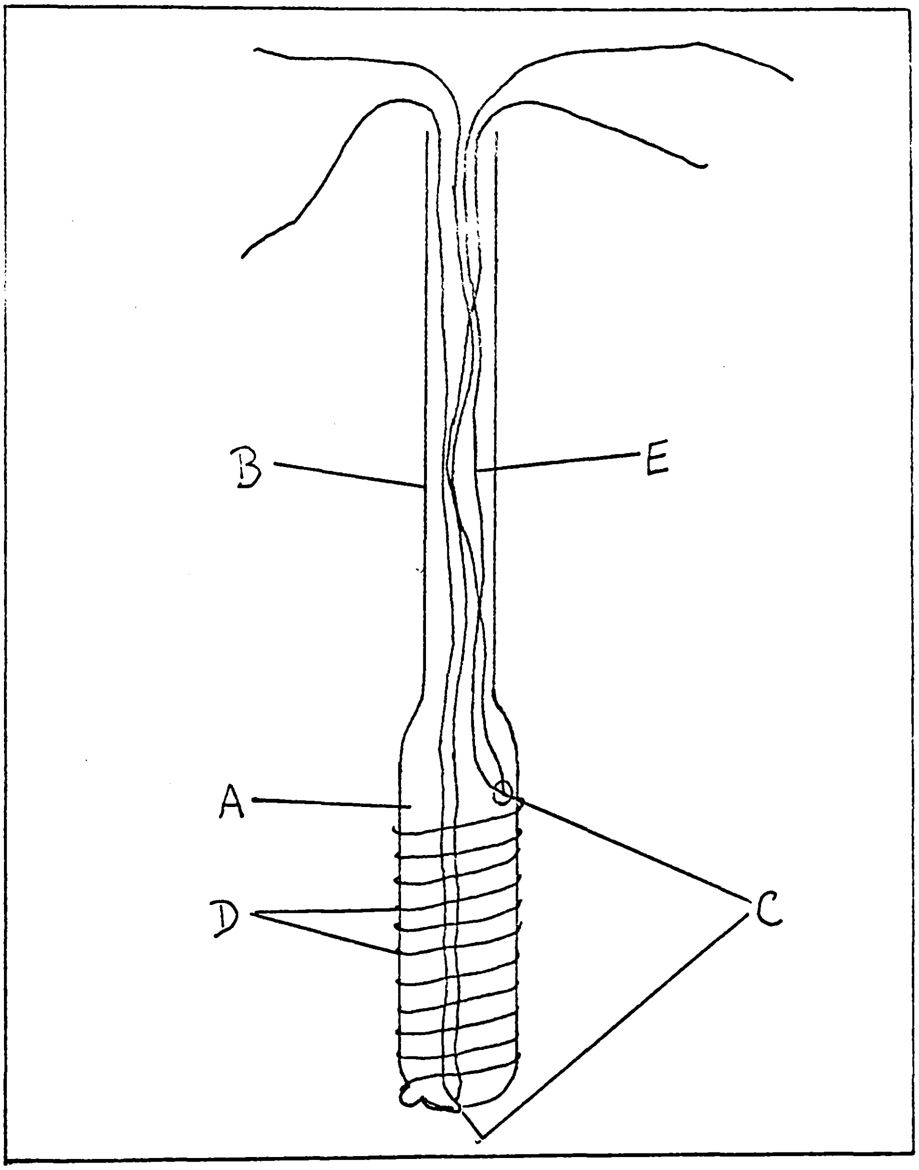


Fig. 14

suspension of araldite in ethanol.

The heating circuit was similar to that of Pitzer[56], and is shown in Figure 15. A variable resistance, A, was used to regulate the current which was measured by determining the voltage drop across a standard 1 ohm resistance, D, using a Cambridge slide-wire potentiometer. By means of a dummy resistance, C, equal to that of the heater, B, the 12 volt battery was allowed to settle down to minimise fluctuations in the current through the heater during heating periods.

The mixing device is shown in Figure 16. It consisted of a glass tube of about 5 ml. capacity, A, which could be sealed at both ends by rubber bungs cemented on to perspex discs, B. The perspex discs were attached to nylon threads, C, which were led out of the calorimeter through the glass supporting tube, D. During an experiment, the contents of the mixing device could be emptied into the Dewar by pulling on the nylon threads.

A pair of matched thermistors, H, in Figure 13, (Stantel, Type F 15 MP) of resistance 100,000 ohms, (Temperature coefficient of resistance 4% per °C.), were used as sensing elements. These were incorporated in the two arms of a Wheatstone bridge, as shown in Figure 17, the other two arms of similar resistance, being high quality Helipot potentiometers. Capacity effects were balanced out by means of two 5-50pF. variable condensers in parallel with the Helipots.

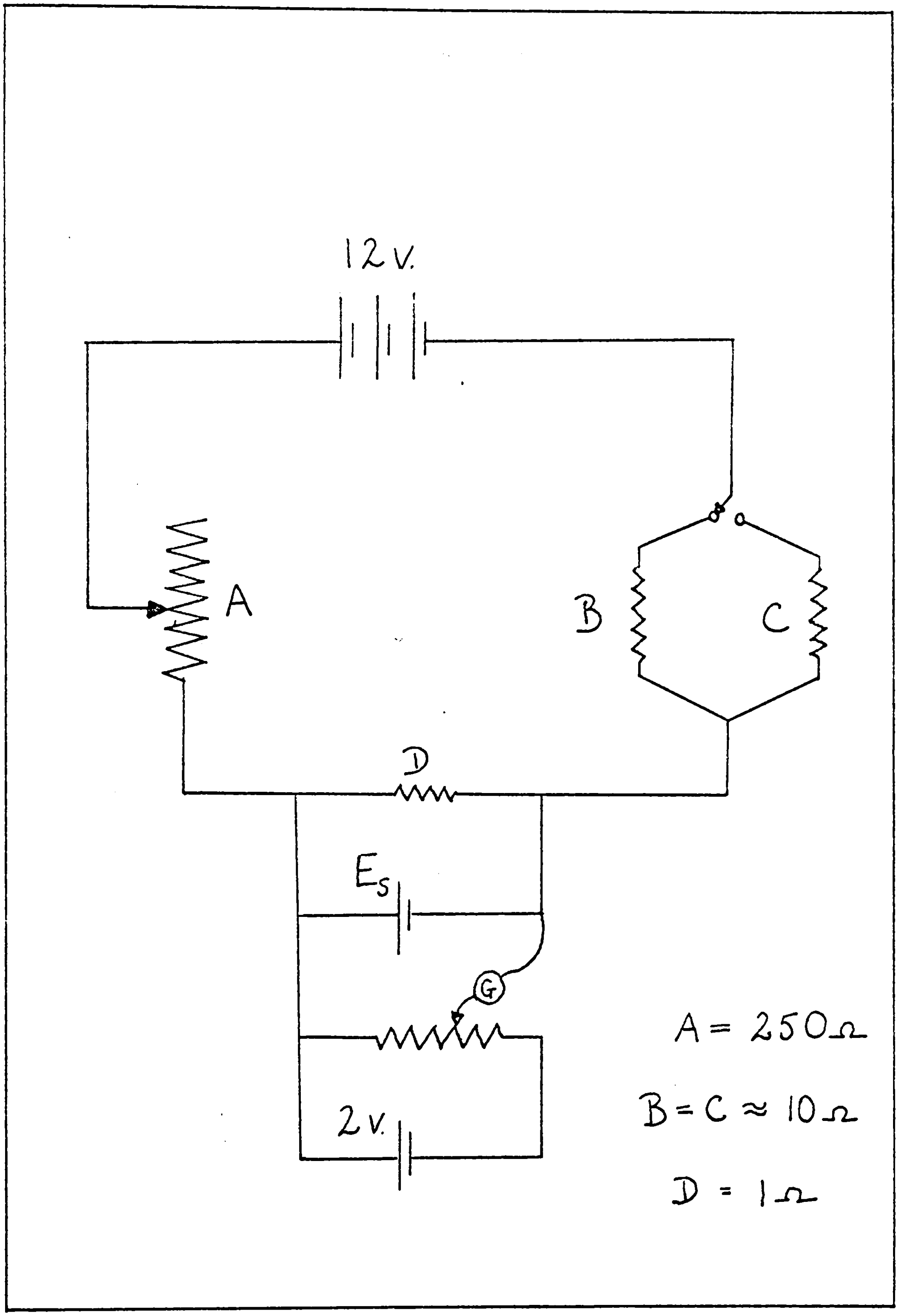


Fig. 15

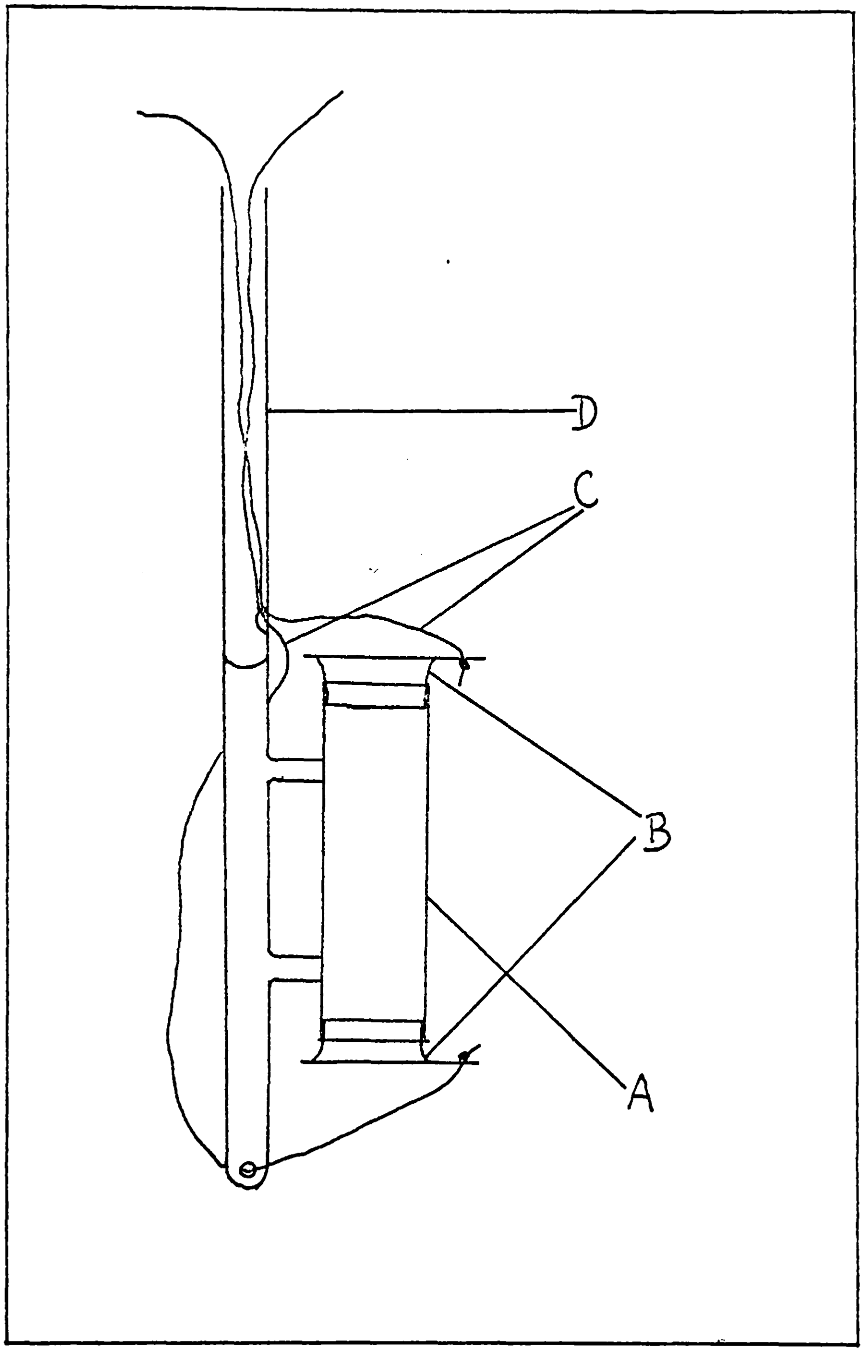


Fig. 16

The bridge was energised by a stabilised 1 volt a.c. signal of frequency 800 c.p.s. The out-of-balance signal was amplified by means of a high gain a.c. amplifier incorporating a phase conscious synchronous detector and the output was rectified and fed to a.d.c. amplifier coupled to a 1 m.v. fast-response chart recorder. A block diagram of the circuit is shown in Figure 17. The sensitivity of the bridge could be varied by means of an adjustable gain control. To test the linearity of the recorded signal, close tolerance 100,000 ohm resistors together with a high quality variable resistor was substituted in place of the thermistors, and Figure 18 shows a typical plot of output signal versus resistance change. Over the range studied, the output was proportional to the resistance difference between the two arms of the bridge and so the signal could be used as a direct meacure of the temperature difference between the calorimeters. The noise level was sufficiently low to enable temperature differences of 10^{-5}°C., corresponding to 3×10^{-3} calories to be detected.

The calorimeters were placed in a large water filled thermostat which was maintained at 25°±0.01°C. by means of a large capacity mercury-toluene regulator in conjunction with a Sunvic proportionating head. The heating element was a 250 watt bulb. A cooling coil was included in the system through which a slow flow of cold water was maintained.

The current was timed by manually operating a Pye stop-clock which was shown to be accurate to within ±0.1%

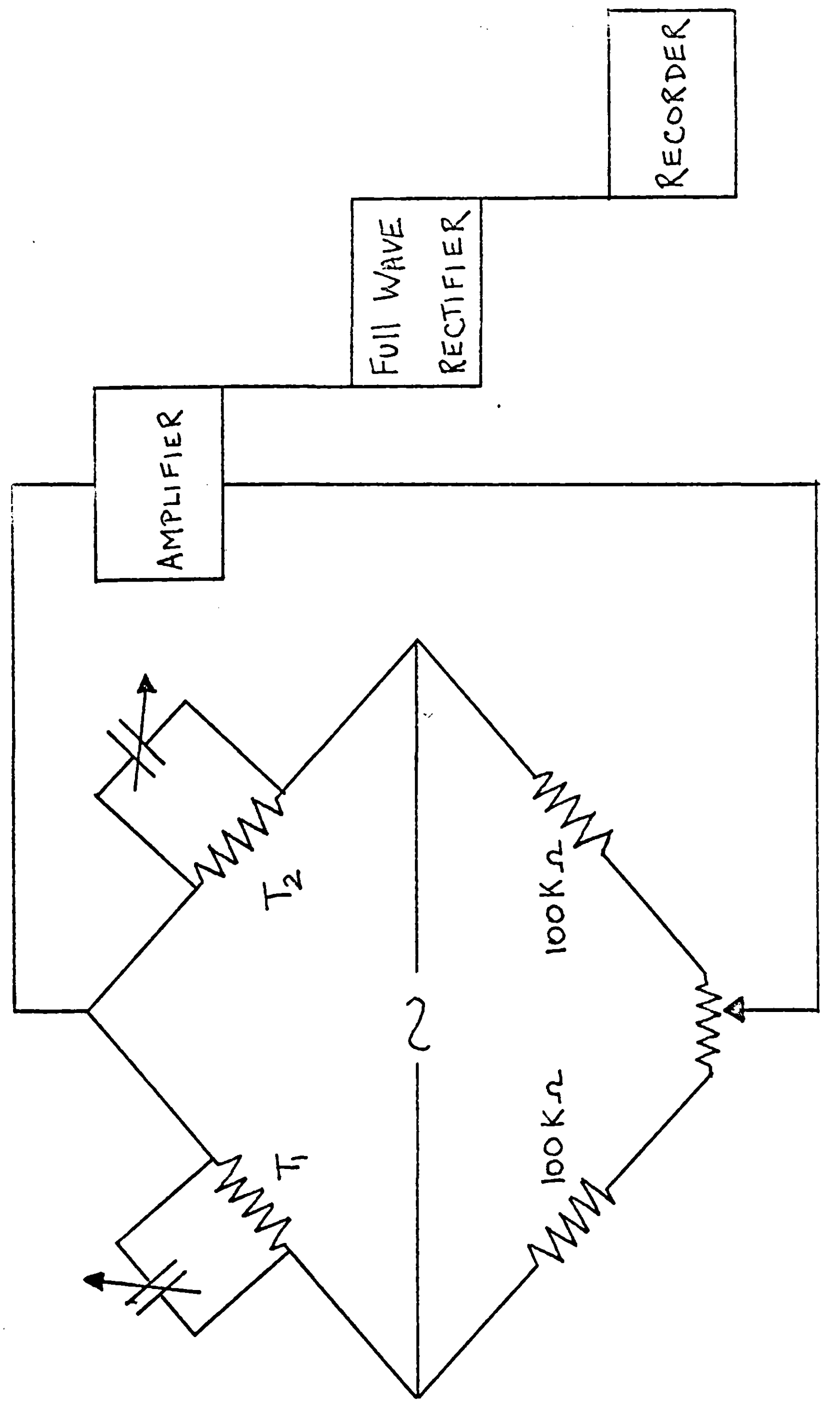


Fig. 17

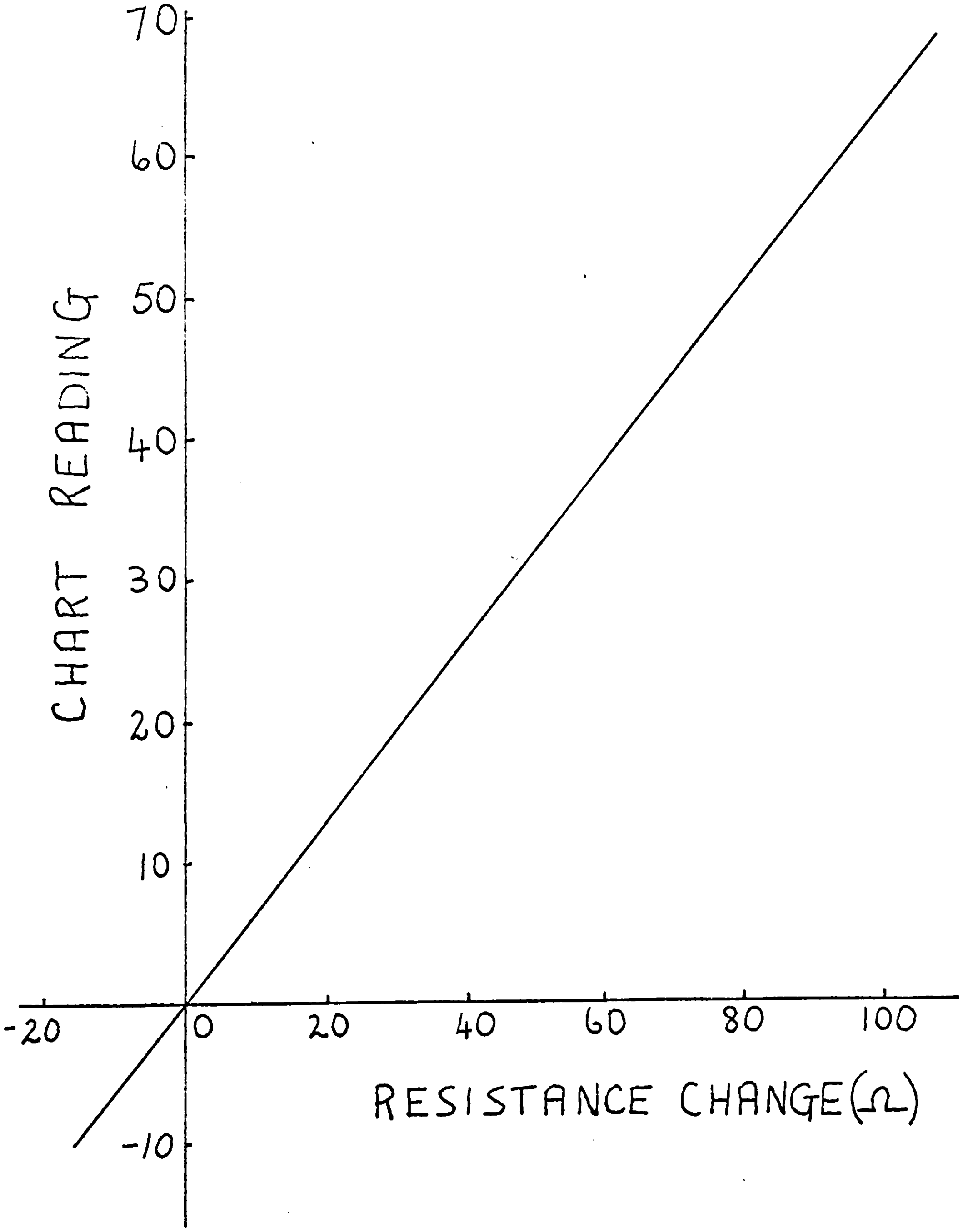


CHART READING
70
60
50
40
30
20
10
-10
-20
0
20
40
60
80
100
RESISTANCE CHANGE(Ω)

Fig. 18

when the heating circuit was designed such that an electric timer , (Ericson Interval Timer), was synchronised with the heater on-off switch.

Experimental Procedure

Equal volumes of solution, 300 ml. at 25°C., were introduced into both calorimeters. The solutions were stirred for at least two hours in the thermostat before each run to ensure equilibration. When a steady change of e.m.f. was established, represented by straight lines on the chart, heat was introduced by switching the heater into the circuit. Current was passed through the heater for about 60 seconds. The voltage drop across the standard 1Ω resistance gave a direct measure of the heating current. After the heater had been switched off and the e.m.f. had settled down to another steady rate of change the mixing device was opened. A rapid change of e.m.f. was observed at this point reflecting the rate of the reaction and when the change in e.m.f. had once again become steady, the water equivalent was again determined by heating electrically.

Calibration of Calorimeters

There are a number of chemical reactions with well authenticated heat changes which have been used to check the calibration of solution calorimeters. Among the most common are (1) the heat of solution of crystalline potassium chloride[62], (2) the heat of reaction of tris-(hydroxymethyl)-amino-methane with hydrochloric acid[63] and (3) the heat of ionisation of water[56, 60, 64, 65, 66, 67].

The heat of ionisation of water was used to test the sensitivity of the calorimeters. The classical method of determining ΔH for the reaction,

$$H^+ + OH^- \rightleftharpoons H_2O \text{ ------------------------ } (41)$$

is to measure the heat of neutralisation of a strong acid with a strong base and values in the literature refer to a variety of ionic strengths and temperatures. Rossini[64] and Pitzer[56] corrected these values to zero ionic strength and 25°C. and recent estimations were carried out at low ionic strength with a refined correction for heat of dilution[68]. It has been shown[60] that the ΔH_0 value is independent of the salt formed in the acid base reaction, an identical result having been obtained with hydrochloric and perchloric acids.

Sodium hydroxide solutions were sealed in the mixing device and the experimental heat change when this was mixed with dilute acid solution in the calorimeters was measured. A stoichiometric excess of base was used to avoid any heat effects from the neutralisation of carbonate in the base.

Determination of the Heats of Complex Formation.

For measurement of the heat of complex formation the Dewars contained solutions of the metal salt. N-methylimino-diacetic acid was accurately weighed into the mixing device and this was dissolved in sufficient potassium hydroxide solution to convert the acid to its di-anionic form, A^{2-}. In the case of the glycine a stock solution of the potassium salt of the anion was prepared and the required volume of this solution was pipetted into the mixing device. All solutions added to the calorimeters or mixing devices were transferred under an atmosphere of nitrogen. The heat of dilution of the metal solutions was assumed to be zero[69], but it was necessary to determine the heats of dilution of the solutions containing the potassium salts of the ligands for each run. This was done by measuring the heat obtained on mixing the same volume of potassium salt of the ligand into a solution of the same ionic strength as that of the metal solution, but without the metal present. The pH of all solutions were measured at the end of each run using a Beckman Research pH meter.

Results

Results of the calibration experiments are given in table XVI. The mean of the values is comparable to those obtained by other workers whose results are summarised in table XVII. From heats of formation of water at an ionic strength of 0.1M, ΔH_I, the thermodynamic heat of formation, ΔH_0, was derived from the equation[70],

$$\Delta H_0 = \Delta H_I + 2.303\ RT^2\ \frac{3}{2}\left\{\frac{1dD}{DdT} + \frac{1}{T}\right\} \log f_1{}^2, \text{---------}(42)$$

in which the values of D, the dielectric constant of water, were those of Akerlof[71].

If an appreciable excess of metal ion was used in the experiments with N-MIDA conditions could be chosen such that only the 1:1 complex, MA, was formed. The concentrations of ionic species were calculated from the quadratic equation,

$$\left[A^{2-}\right]^2\left\{K_1\left(1 + \frac{\left[H^+\right]}{k_2}\right)\right\} + \left[A^{2-}\right]\left\{1 + \frac{\left[H^+\right]}{k_2} + K_1(Tm - Ta)\right\} = Ta, \text{---------}(43)$$

derived from equations for total acid,

$$Ta = \left[HA^-\right] + \left[A^{2-}\right] + \left[MA\right] \text{------------------------}(44)$$

total metal

$$Tm = \left[M^{2+}\right] + \left[MA\right], \text{------------------------}(45)$$

k_2 for the acid, equation (21), and K_1 for the complex, equation (29). For these solutions in which the metal ion concentration was high MOH^+ was formed in experiments involving magnesium and calcium ions. Modifying equation (44) to include a term in $\left[MOH^+\right]$ and knowing the association constant for MOH^+, equation (40), for this ion the quadratic equation,

$$\left[A^{2-}\right]^2\left\{K_1(H + k2)\right\} + \left[A^{2-}\right]\left\{k_2K_1(Tm - Ta) + \left[H^+\right](1 + k_h\left[OH^-\right])\right\}$$
$$+ \; k_2(1 - k_h\left[OH^-\right]) = Ta.k_2(1 + k_h.\left[OH^-\right])\text{-------}(46)$$

was derived and solved for A^- from which the concentrations of all other species could be derived.

In solutions in which two complexes, MA and MA_2^{2-}, existed together, a cubic expression derived from equations (21),(26),(27),(29),(30),

$$\left[A^{2-}\right]^3\left\{K_1K_2(1 + \frac{\left[H^+\right]}{k_2})\right\} + \left[A^{2-}\right]^2\left\{K_1K_2(2Tm - Ta) + K_1(1 + \frac{\left[H^+\right]}{k_2})\right\}$$
$$+ \left[A^{2-}\right]\left\{K_1(Tm - Ta) + 1 + \frac{\left[H^+\right]}{K_2}\right\} = Ta,\text{--------------}(47)$$

resulted. The concentrations of species were obtained by solving this equation. Results of these calculations for N-MIDA are given in tables (XVIII-XX111) and for similar calculations for glycine in tables XXIV and XXV. A 7044 'Fortran' computer was programmed for carrying out these calculations.

Evaluation of heat Changes

The method used for the evaluation of water equivalents and the heats of formation was that of Eitel[72]. In Figure 19, which is a graphical reproduction of a typical chart trace for a water equivalent determination, chart reading is plotted against time. This was divided into three periods, the Anterior, the Experimental and the Rating periods. The first reading was designated θ_o at time T_o, and at T_i, where the reading was θ_i, the heater, was switched on. The rate of change, Va, was given by $(\theta_o - \theta_i)/(T_i - T_o)$divs. t^{-1} and the average reading in this period was $\theta_a = \frac{1}{2}(\theta_o + \theta_i)$divs. The heat change was given by a change in chart reading from θ_i to θ_e, where θ_e marks the commencement of the Rating period and θ_l its termination, the corresponding times being T_e and T_l. The rate of change, V_r, and the average reading θ_r, in this period were given by $(\theta_e - \theta_l)/(T_l - T_e)$divs. t^{-1} and $\frac{1}{2}(\theta_e + \theta_l)$ divs. respectively.

The Reynault-Pfaundler formula was then applied to correct the experimental heat change for any variation in slopes of the Anterior and Rating periods. The correction applied to $(\theta_e - \theta_i)$divs. was

$$\delta\theta = T_x V_a + (V_r - V_a)/(\theta_r - \theta_a).\left\{\tfrac{1}{2}(\theta_e + \theta_i) + \sum_{T_i}^{T_e - 1}\theta - T_x\theta_a\right\}$$

and the corrected heat change was given by,

$$\Delta\theta = (\delta\theta + \theta_e - \theta_i)\text{divs.}$$

Multiplication of $\Delta\theta$ divs. by the water equivalent (in cals/-chart div.) gave the experimental heat change, $-Q$ cals.

The measured heat change, Q, was expressed by,

$$Q = Q^1 + q(1) + q(2) + q(3) \quad \text{------------------------------} (48)$$

where Q^1 was the contribution from the heat of complex formation, q(1), the heat of dilution of the potassium salt of the acid, q(2), the heat due to formation of water and q(3), the heat contribution from changes in the ligand/ proton equilibrium. The value of q(1) was obtained from a blank run carried out for each experiment.

Knowing the pH of the blank solutions, pH_B, concentrations

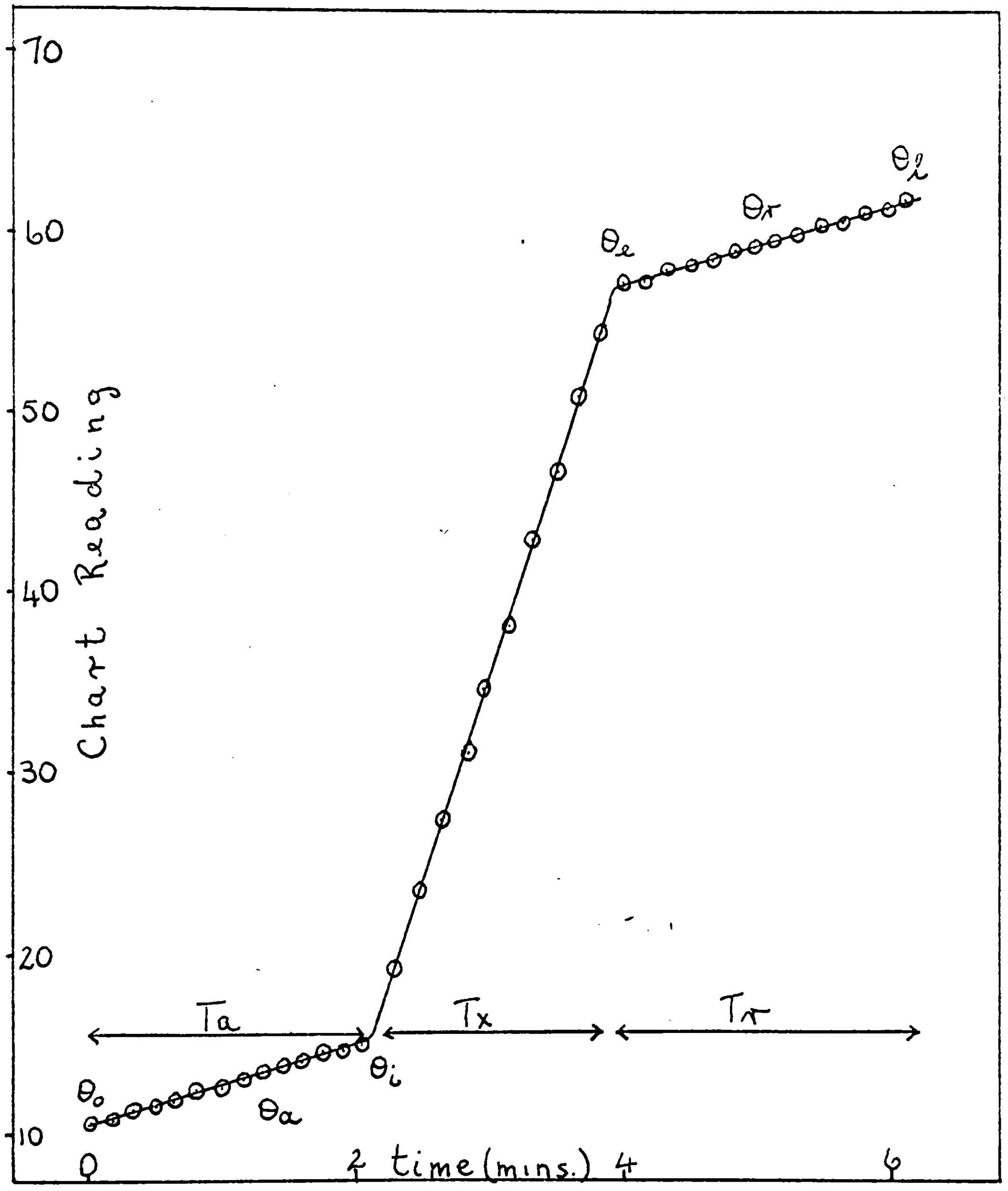


Chart Reading
70
60
50
40
30
20
10
0
2
time (mins.)
4
6
Ta
Tx
Tr
θo
θa
θi
θe
θr
θl

Fig 19

of the acid species $[A^{2-}]_B$ and $[HA^-]_B$ for N-MIDA and $[G^-]_B$ and $[HG]_B$ for glycine were calculated from the dissociation constants for the acids, equations (21) and (35) respectively, and from the expression for total acid, equation (22). The corresponding concentrations in the metal complexing experiments were calculated by the method described previously. Heat contributions, q(3) were evaluated from the appropriate heats of protonation,

$$A^{2-} + H^+ = HA^-, \quad \Delta H_{Ass.} = -6.8 \text{ k.cal.mole}^{-1}\,{}^{73}.$$

for N-MIDA and,

$$G^- + H^+ = HG, \Delta H_{Ass.} = -10.80 \text{ k.cals.mole}^{-1}\,{}^{74}.$$

for glycine.

The heat contribution, q(2), was calculated from pH_B and pH_C (the pH of the solution containing the complex) using a value 13.36 k.cal.mole^{-1} recommended by Staveley[57], for the heat of formation of water.

With a knowledge of q(1), q(2) and q(3) the experimental heat due to complex formation, Q^1, was calculated from equation (47). The heat of complex formation, $\bar{\Delta H_I}$ k.cal.mole^{-1}, was then calculated for an ionic strength of 0.1. In cases where both MA and MA_2, were present, the ΔH_1 and ΔH_2 were obtained by solving simultaneous equations. The enthalpy of formation of $MgOH^+$ had not been previously determined but from a consideration of the values for Ca, Sr and Ba[75] and a knowledge of the trends shown by other anions with these metals a value of 2.8 k.cal.mole.$^{-1}$ was assumed in order to estimate the small corrections required. Gimblett and Monk's[75] value of 1.25

k.cal.mole^{-1}. for the enthalpy of formation of $CaOH^+$ was used to make corrections in experiments in which this ion-pair was formed.

Results of these calculations for N-MIDA are given in tables (XVIII-XXIII) and for glycine in tables XXIV and XXV.

TABLE XVI

Calorimeter 1.

Run	$-Q$ (cal.)	$-\Delta H_I$ (k.cal.mole^{-1}.)	δ cal.	$-\Delta H_o$ (k.cal.mole^{-1}.)
1	5.47	13.10	38	13.06
2	5.56	13.31	38	13.27
3	5.57	13.34	36	13.30
4	4.33	13.83	33	13.80
5	5.54	13.27	36	13.23

Mean $\Delta H_o = 13.33 \pm 0.19$ k.cal.mole^{-1}.

Calorimeter 2.

Run	$-Q$ (Cal.)	$-\Delta H_I$ (k.cal.mole^{-1}.)	δ cal.	$-\Delta H_o$ (k.cal.mole^{-1})
1	4.15	13.25	32	13.23
2	4.28	13.68	38	13.64
3	4.12	13.12	32	13.08
4	5.57	13.34	36	13.30
5	5.60	13.40	36	13.36

Mean $\Delta H_o = 13.32 \pm 0.14$ k.cal.mole^{-1}.

TABLE XVII

Heat of Ionisation of Water

Reaction	$-\Delta H_o$ (k.cal.mole^{-1}.)	Ref.
HCl + NaOH	13.363	56
HCl + NaOH	13.320	65
HCl + NaOH	13.336	66
HCl + NaOH	13.356	57
$HClO_4$ + NaOH	13.334	67
$HClO_4$ + NaOH	13.335	60
HCl + NaOH	13.340	60
$HClO_4$ + NaOH	13.325	This work.

TABLE XVIII

Heat of Formation of the Magnesium N-Methyliminodiacetate Complex, MA.

Run	$Tm.10^2$	$Ta.10^3$	pH	$[MA].10^3$	$[MOH^+].10^4$
1	2.758	3.159	9.628	3.070	1.888
2	2.758	3.154	9.619	3.065	1.849
3	2.758	3.154	9.654	3.068	2.004
4	1.931	3.161	9.757	3.046	1.688
5	1.931	3.159	9.806	3.050	1.890
6	1.931	3.161	9.671	3.036	1.390

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal. $unit^{-1}$)	-Q (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. $mole^{-1}$)
1	300	15.60	.153	-2.392	-2.937	2.87
2	300	9.55	.226	-2.185	-2.759	2.70
3	300	12.25	.188	-2.303	-2.874	2.81
4	300	10.90	.210	-2.292	-2.833	2.79
5	300	12.70	.195	-2.470	-2.959	2.91
6	300	10.70	.220	-2.357	-3.026	2.99

mean $\Delta H_I = 2.85 \pm .08$ k.cal.mole^{-1}.

TABLE XIX

Heat of Formation of the Calcium N-Methyliminodiacetate Complex, MA

Run	$T_m.10^2$	$T_a.10^3$	pH	$[MA].10^3$
1	1.973	2.808	9.777	2.767
2	1.973	2.802	9.329	2.728
3	1.973	3.156	9.878	3.113
4	1.480	3.159	9.874	3.101
5	1.973	3.150	9.878	3.106
6	1.480	3.152	9.958	3.095
7	1.973	3.152	9.861	3.108

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal. unit^{-1})	$-Q$ (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. mole^{-1}.)
1	300	8.50	.161	1.372	0.929	-1.12
2	300	6.00	.157	0.939	0.856	-1.05
3	300	9.05	.166	1.504	1.267	-1.36
4	300	6.55	.197	1.288	1.033	-1.11
5	300	15.35	.102	1.566	1.219	-1.31
6	300	14.75	.103	1.512	1.239	-1.33
7	300	13.33	.101	1.345	1.088	-1.05

Mean $\Delta H_I = -1.19 \pm .12$ k.cal.mole^{-1}.

TABLE XX

Heat of Formation of the Strontium N-Methyliminodiacetate Complex, MA

Run	$T_m.10^2$	$T_a.10^3$	pH	$[MA].10^3$
1	3.289	2.963	9.771	2.777
2	3.289	2.981	9.720	2.784
3	2.000	3.019	9.962	2.749
4	2.000	3.019	9.970	2.750
5	2.000	3.020	9.953	2.748
6	2.000	3.020	9.983	2.754

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal. $unit^{-1}$)	$-Q$ (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. $mole^{-1}$.)
1	300	11.80	.100	1.185	.833	-0.90
2	300	11.50	.104	1.195	.789	-0.85
3	300	9.10	.098	0.895	.664	-0.81
4	300	9.00	.105	0.941	.722	-0.87
5	300	7.80	.105	0.815	.570	-0.69
6	300	8.25	.111	0.916	.717	-0.87

Mean $\Delta H_I = -.83 \pm .06$ k.cal.mole^{-1}.

TABLE XXI

Heat of Formation of the Barium N-Methyliminodiacetate Complex, MA.

Run	Tm.10^2	Ta.10^3	pH	[MA].10^3
1	2.000	3.019	10.171	2.543
2	2.000	3.024	9.991	2.499
3	2.667	3.016	10.082	2.637
4	2.667	3.016	10.150	2.651
5	2.667	3.022	10.231	2.669
6	2.667	3.019	10.104	2.645

Run	Total Vol. (ml.)	$\Delta\theta$ (Units)	W.E. (cal. unit^{-1})	$-Q$ (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. mole^{-1}.)
1	300	11.03	.075	.825	0.841	-1.10
2	300	8.00	.106	.847	0.789	-1.05
3	300	5.75	.126	.726	0.618	-0.78
4	300	6.55	.125	.819	0.848	-1.07
5	300	6.45	.148	.953	0.984	-1.23
6	300	6.70	.145	.974	0.909	-1.15

Mean $\Delta H_I = -1.06 \pm 0.10$ k.cal.mole^{-1}.

TABLE XXII

Heat of Formation of the 1:2 Magnesium N-Methyliminodiacetate Complex, MA_2^{2-}

Run	$Tm.10^3$	$Ta.10^3$	pH	$[MA].10^3$	$[MA_2^{2-}].10^3$
1	2.758	8.277	10.763	1.382	1.262
2	2.758	8.286	10.737	1.384	1.260
3	3.310	8.279	10.736	1.768	1.370
4	2.758	8.274	10.684	1.385	1.259
5	3.310	8.288	10.665	1.769	1.369

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal. $units^{-1}$)	-Q (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. $mole^{-1}$.)
1	300	33.45	.090	-3.024	-.876	2.31
2	300	27.80	.097	-2.699	-.813	2.15
3	300	17.90	.150	-2.692	-.747	1.82
4	300	19.95	.145	-2.893	-1.013	2.68
5	300	17.70	.146	-2.582	-.805	1.96

Mean $\Delta H_I = 2.18 \pm .27$ $k.cal.mole^{-1}$.

TABLE XXIII

Heat of Formation of the 1:2 Calcium N-Methyliminodiacetate Complex, MA_2^{2-}.

Run	$Tm.10^3$	$Ta.10^3$	pH	$[MA].10^4$	$[MA_2^{2-}].10^3$
1	2.960	8.272	10.655	9.777	1.938
2	2.960	8.278	10.660	9.839	1.931
3	3.552	8.290	10.590	13.720	2.099
4	3.552	8.272	10.598	13.750	2.096
5	2.565	8.279	10.670	7.721	1.763
6	3.552	8.276	10.613	13.720	2.100
7	2.565	8.270	10.662	7.739	1.761

Run	Total vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal. units^{-1})	$-Q$ (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. mole^{-1}.)
1	300	12.10	.124	1.505	1.465	-2.52
2	300	9.65	.123	1.190	1.184	-2.04
3	300	12.80	.124	1.582	1.138	-1.81
4	300	11.60	.123	0.896	0.972	-1.55
5	300	8.80	.122	1.074	1.060	-2.00
6	300	11.65	.128	1.488	1.185	-1.88
7	300	7.70	.128	0.986	0.916	-1.73

Mean $\Delta H_I = -1.93 \pm .22$ k.cal.mole^{-1}

TABLE XXIV

Heat of Formation of the Magnesium Glycinate Complex, MG^+.

Run	$Tm.10^2$	$Ta.10^3$	pH	$[MG^+].10^4$	$[MOH^+].10^4$
1	1.695	3.752	10.172	7.189	4.282
2	1.017	3.752	10.320	4.933	3.557
3	0.509	3.752	10.395	2.699	2.088
4	2.758	3.000	10.134	8.233	6.213
5	1.379	3.000	10.235	5.024	4.043

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal. $unit^{-1}$.)	$-Q$ (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. $mole^{-1}$.)
1	300	3.50	.103	-0.359	-1.737	7.25
2	300	1.73	.234	-0.419	-1.145	6.97
3	300	2.44	.098	-0.239	-0.694	7.56
4	300	8.50	.103	-0.876	-1.847	6.73
5	300	4.50	.106	-0.479	-1.146	6.85

Mean $\Delta H_I = 7.07 \pm 0.27$ k.cal.mole^{-1}.

TABLE XXV

Heat of Formation of the Calcium Glycinate Complex, MG^+

Run	$Tm.10^2$	$Ta.10^3$	pH	$[MG^+].10^4$	$[MOH^+].10^5$
1	1.973	3.000	10.400	3.800	5.480
2	1.973	3.000	10.410	3.804	5.590
3	1.973	3.000	10.406	3.800	5.540
4	2.960	3.000	10.353	5.280	7.380

Run	Total Vol. (ml.)	$\Delta\theta$ (units)	W.E. (cal. $unit^{-1}$)	$-Q$ (cal.)	$-Q^1$ (cal.)	ΔH_I (k.cal. $mole^{-1}$.)
1	300	3.30	.069	-0.229	-.947	2.31
2	300	1.40	.103	-0.145	-.342	0.72
3	300	2.00	.103	-.207	-.623	1.46
4	300	0.80	.103	-.083	-.362	0.51

Mean $\Delta H_I = 1.25 \pm 0.64$ k.cal.mole^{-1}.

DISCUSSION

The thermodynamic functions for the 1:1 alkaline earth complexes with N-methyliminodiacetic acid and glycine are given in table (XXVI). Since this work was done, calorimetric results have been published by Anderegg[76] at 20°C. for a number of N-MIDA complexes. The values are given in brackets in table (XXVI) and the agreement, in most cases, with the present work is seen to be satisfactory. The table also includes values for iminodiacetic acid[77] and nitrilotriacetic acid[78] and, in order to facilitate comparisons, the data are plotted as a function of atomic number in Figure (20).

The entropy change accompanying the reaction,

$$M(H_2O)_x^{2+} + A(H_2O)_y^{2-} \rightleftharpoons MA(H_2O)_z + (x-y-z)H_2O \text{-------}(49)$$

can be considered to be made up of two parts, a decrease in entropy due to the reduction of the number of solute species in solution and an increase due to the greater mobility of solvent molecules brought about by charge neutralisation. Frank and Evans[79] have suggested that ions in solution orientate the water molecules around them so as to form an effective "iceberg", the process being similar to partial freezing of the liquid. The removal of ions from the solution, as in the process of complex formation, will lead to a breakdown of this structure and a resulting positive entropy change,

TABLE XXVI

Thermodynamic Functions for Metal Complex Formation.

Reaction	$-\Delta G$ (k.cal.mole^{-1})	ΔH (k.cal.mole^{-1})	ΔS (cal.deg^{-1}mole^{-1})
Mg^{2+} - $MIDA^{2-}$	4.78 (4.62)	+2.85 (+3.12)	25.6 (26.4)
Ca^{2+} - $MIDA^{2-}$	5.25 (5.03)	-1.19 (-1.64)	13.6 (11.58)
Sr^{2+} - $MIDA^{2-}$	4.02 (3.82)	-0.83 (-1.23)	10.7 (8.85)
Ba^{2+} - $MIDA^{2-}$	3.56 (3.47)	-1.06 (-0.79)	8.4 (9.17)
Mg^{2+} - gly^{-}	1.80	+7.07	29.8
Ca^{2+} - gly^{-}	1.31	+1.25	8.6
Mg^{2+} - IDA^{2-}	3.94	+2.94	23.5
Ca^{2+} - IDA^{2-}	3.47	+0.30	12.7
Sr^{2+} - IDA^{2-}	2.99	+0.10	10.5
Ba^{2+} - IDA^{2-}	2.24	+0.10	8.0
Mg^{2+} - NTA^{3-}	7.25	+4.44	39.8
Ca^{2+} - NTA^{3-}	8.60	-1.36	24.7
Sr^{2+} - NTA^{3-}	6.68	-0.54	20.9
Ba^{2+} - NTA^{3-}	6.44	-1.44	17.1

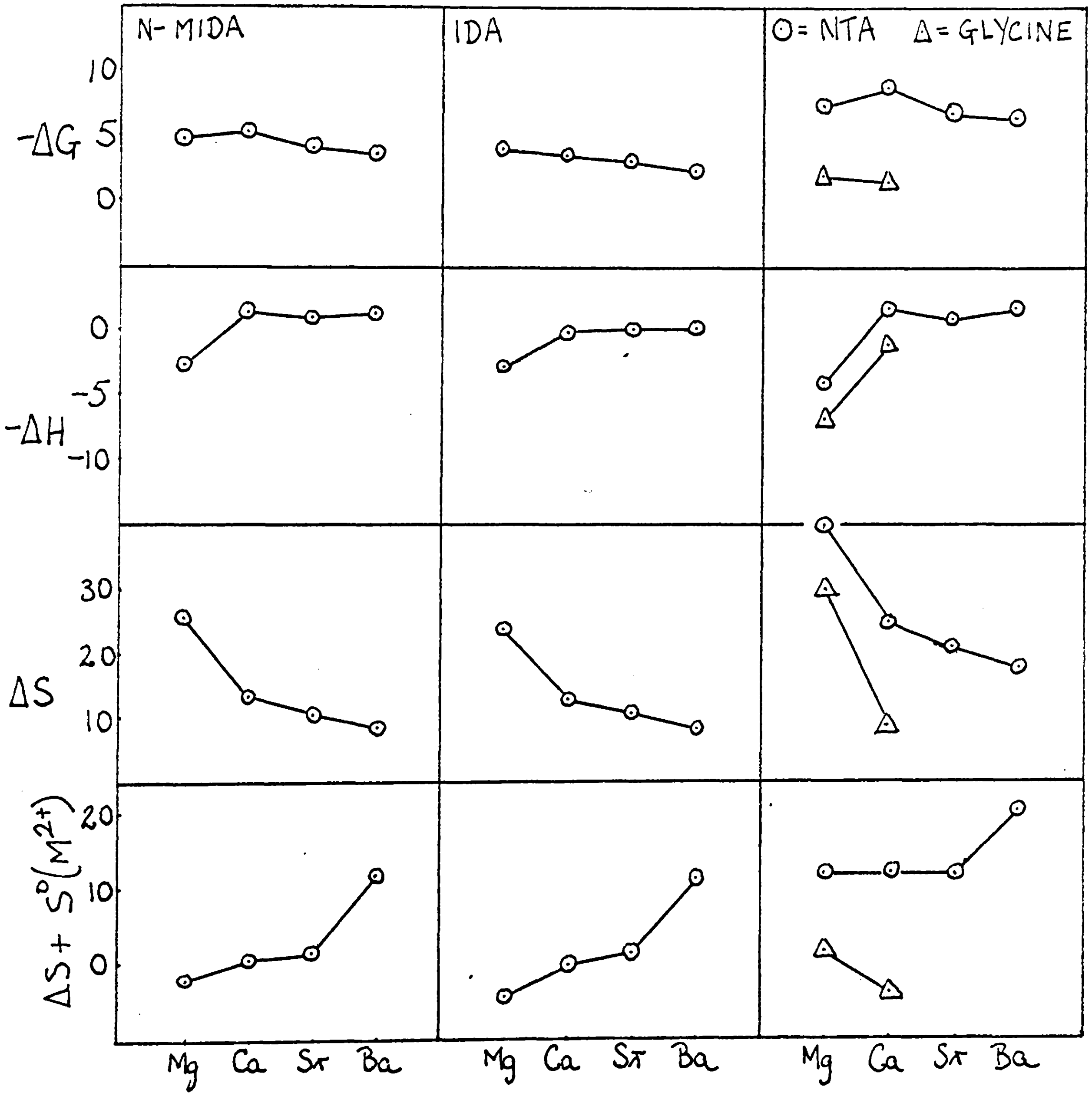

N- MIDA
IDA
O = NTA
Δ = GLYCINE
-ΔG
10
5
0
-ΔH
0
-5
-10
ΔS
30
20
10
ΔS + S°(M2+)
20
10
0
Mg
Ca
Sr
Ba
Mg
Ca
Sr
Ba
Mg
Ca
Sr
Ba

Fig. 20

ΔS, favouring the reaction. Since the entropy effect will be related to the ionic charges and the degree of hydration of the ions, a large positive ΔS will be expected in reactions involving metal ions with low hydration entropies which undergo efficient charge neutralisation in forming complexes.

The entropy change accompanying the ion association reaction (49),

$$\Delta S = S^{o}(MA) - S^{o}(M^{2+}) - S^{o}(A^{2-}), \text{------------------} (50)$$

where S^{o} is the standard aqueous entropy of the species enclosed in brackets, can be written as a sum of hydration, ΔS_{hyd}, and gas phase, S_g, entropies, resulting in the equation,

$$\Delta S + S^{o}(M^{2+}) = \underbrace{\Big[S_g(MA) - S_g(A^{2-})\Big]}_{I} + \underbrace{\Big[\Delta S_{hyd}(MA) - \Delta S_{hyd}(A^{2-})\Big]}_{II} \text{----} (51$$

Values of $\Delta S + S^{o}(M^{2+})$ are given in table XXVII for the complexes involving N-MIDA and glycine at 25°C. and for all the other aminocarboxylate complexes for which accurate calorimetric data are available. For the most part the latter have been obtained from calorimetric measurements at 20°C. but the temperature difference between 20 and 25°C. will not affect the following arguments.

TABLE XXVII

Values of $\Delta S + S^{o}(M^{2+})$ for 1:1 Metal Aminocarboxylate Complexes

Metal Ion	MIDA	GLYC.	IDA[77]	EDTA[80,81]	NTA[78]
Mg^{2+}	-2.6	+1.6	-4.7	22.8	11.6
Ca^{2+}	+0.4	-4.61	-0.5	13.4	11.5
Sr^{2+}	+1.3		1.1	16.2	11.5
Ba^{2+}	+11.4		11.0	21.7	20.1

In equation (51), term I reflects the change in configurational and librational entropy of the ligand molecule when it enters into complex formation. The translational component of this term will be small, and, since the ligand loses some of its mobility, in forming a more rigid complex, term I will be expected to be negative. Term II on the other hand will be positive since $\Delta S_{hyd}(A^{2-})$ will be more negative than $\Delta S_{hyd}(MA)$ in which the charge has been neutralised. For a series of complex formation reactions involving the same ligand, $S_{g}(MA)$ will not vary appreciably so that $\Delta S + S^{o}(M^{2+})$ will reflect the hydration entropies of the complexes. The absence of any large differences in the values of $\Delta S + S^{o}(M^{2+})$ for magnesium, calcium and strontium, indicates a similar structure for their complexes. A common feature of the data, however, is the relatively high $\Delta S + S^{o}(M^{2+})$ values for the barium complexes. The large barium ion has a small charge density and will bond less effectively to the ligand thus allowing the latter to retain some of its librational entropy in the complex. Consequently, term I will be smaller than for complexes involving other metal ions. In addition the barium ion in its complexes might be expected to retain some of the structure of the free ion due to the inability of the ligand to completely surround the large metal ion. If this is the case the S^o of the complex will be similar to the S^o for the Ba^{2+} ion which is relatively high.

Where $\Delta S + S^o(M^{2+})$ has large positive values, term II is more important. This is seen to be the case with ethylenediaminetetra-acetic acid (EDTA) and nitrilotriacetic acid (NTA) where the high charged anions, $A^{(4 \text{ or } 3)-}$ respectively, have very small hydration entropies compared to $\Delta S_{hyd}(MA)$ since a large degree of charge neutralisation will have occurred in forming the complex. In most of the other cases in table XXVII terms I and II are about equally important.

Since the divalent alkaline earth ions have inert gas electronic configurations they will be expected to form essentially ionic bonds in their complexes with ligands. There is some evidence[45], however, which suggests that a certain degree of covalency is present, especially in bonds between nitrogen and the magnesium ion. It is clear from the N.M.R. evidence, presented in Part I, that the magnesium and calcium ions bond to the nitrogen coordination centre of N-MIDA and it is difficult to conceive of a strong bond which is purely ionic in character. Further evidence for nitrogen bonding may be seen from the enhanced stability of N-MIDA and IDA complexes over those formed with the analogous dicarboxylic acid having a CH_2 group in place of the nitrogen. If electrostatic interactions were the only factor to be considered then the magnesium complex would be expected to have a greater stability than that of the calcium. This is not the case for the N-MIDA and NTA complexes in table XXVI and a number of other polyaminopolycarboxylate ligands are known which show the same behaviour in their complexes with magnesium and calcium ions.

It is preferable to consider the free energy change as being a consequence of heat and entropy changes and to discuss both of these functions. It is seen in table XXVI that all the magnesium complexes form with an endothermic heat change and a large positive entropy change. This large increase in entropy is a result of the high charge density of the small magnesium ion which causes it to have a relatively small aqueous entropy leading to a large ΔS when it associates with negatively charged ligands. The endothermic heat change is probably a result of two effects: (1) that the energy required to break the relatively strong magnesium-water bonds outweighs the energy returned to the system when the metal-ligand bonds are formed and (2) the endothermicity involved in the formation of strained $N\text{-}CH_2\text{-}COO^-$ chelate rings around the small magnesium ion. Molecular models indicate that the strain is greatest for the magnesium ion and smallest for the calcium ion. The stability of these complexes which absorb heat when they are formed is thus a consequence of the very large increase in entropy accompanying the process.

The effect of introducing a methyl group on the nitrogen for N-MIDA as compared with IDA is seen from the heats of formation of the two series of complexes in table XXVI. The greater exothermicity of the N-MIDA complexes can be attributed to the inductive effect of the methyl group in enhancing the bonding of the nitrogen to the metal ion. In contrast to N-MIDA the magnesium complexes of IDA are more stable than the calcium. The calcium complex of IDA is formed with a more endothermic heat change than is the N-MIDA complex while the heat change for the formation of the magnesium complexes is almost the same for both of the ligands. These results can be explained if a relatively stronger covalent bond is formed between the magnesium ion and the nitrogen atoms than that involving the calcium ion. This would be expected to be less enhanced by the inductive effect than is the calcium-nitrogen bond and N.M.R. results appear to support this idea.

The stabilities of the calcium, strontium and barium complexes of N-MIDA decrease in the order Ca>Sr>Ba as expected from the electrostatic potentials of the cations. In table XXVI however, it can be seen that the heat of formation of the Ba complex is more exothermic than that of the strontium complex. Anderegg's values show the reverse effect but these are contrary to results obtained for NTA in table XXVI and other polyaminopolycarboxylates[78,80,82]. This relatively large exothermic heat of formation of Ba complexes, is probably due to incomplete dehydration of the large ion when it forms complexes resulting in less heat being absorbed in breaking metal-water bonds.

Heat is absorbed in the formation of both the Mg and Ca monoglycinate complexes; the formation of the magnesium complex being much more endothermic. The general trend in this respect is therefore the same as for the other ligands. The greater endothermicity for formation of both of these complexes as compared with those of N-MIDA or IDA reflects the difference in dentate character of the ligands. The heat absorbed in dehydrating the Mg^{2+} and Ca^{2+} ions must be more important than the heat regained by bond formation to the bidentate ligand. Additional evidence for extensive dehydration of the Mg^{2+} ion in formation of its mono-complexes is the fact that the formation of $Mg(MIDA)_2^{2-}$ from Mg(MIDA) takes place with an exothermic heat change. This indicates that most of the water is released from the hydrated magnesium ion in the mono-MIDA complex. It is interesting to note that this ΔH value is almost the same as that accompanying formation of the magnesium EDTA complex. The large entropy change in the formation of magnesium mono-glycinate as compared with the other ligands, may be due to the smaller gas entropy of the glycinate ion in making term I less negative. N-MIDA constitutes one half of an EDTA molecule and as such is ideal for discussion of the chelate effect. The thermodynamic properties for the reaction,

$$M(MIDA)_2^{2-} + EDTA^{4-} \rightleftharpoons MEDTA^{2-} + 2MIDA^{2-}, \text{---------}(52)$$

in which two ligands are replaced by EDTA are given in table XXVIII which also includes data for Zn^{2+} and Cd^{2+} obtained recently by Anderegg[76].

TABLE XXVIII

Thermodynamic Functions for Metal Complex Formation

Reaction	$-\Delta G$ (k.cal.mole^{-1})	ΔH (k.cal.mole^{-1})	ΔS (cal.deg^{-1}mole^{-1})
$MgMIDA + MIDA^{2-}$	3.22	-0.67	8.6
$CaMIDA + MIDA^{2-}$	3.83	-0.74	10.3
$Zn^{2+} + MIDA^{2-}$	10.28	-2.17	27.7
$Cd^{2+} + MIDA^{2-}$	9.08	-1.89	24.5
$ZnMIDA + MIDA^{2-}$	8.62	-3.68	16.7
$CdMIDA + MIDA^{2-}$	7.72	-5.38	8.0

The outer electronic configurations for zinc and cadmium are $3d^{10}4s^2$ and $4d^{10}5s^2$ respectively so that the divalent ions have a filled d shell. It would therefore be expected that these ions would form predominantly ionic bonds. The ionic radii, as given by Pauling[83], 0.74Å for Zn^{2+} and 0.97Å for Cd^{2+}, are sufficiently similar to those for Mg^{2+}, 0.65Å, and Ca^{2+}, 0.99Å, for comparisons to be made.

Schwarzenbach[27] defined the chelate effect of reaction (52),

$$\text{Chel} = \log K_1(\text{EDTA}) - \log K_1K_2(\text{N-MIDA}) \text{-------------} (53)$$

The availability of precise heat and entropy data makes it possible to examine the source of the chelate effect in more detail than is possible from a consideration only of the free energy changes. The entropy change accompanying reaction (52)

$$\Delta S_{chel} = 2S^o(\text{MIDA}) + S^o(\text{MEDTA}) - S^o(\text{EDTA}) - S^o\left[\text{M}(\text{MIDA})_2\right] \text{---} (54)$$

or,

$$\Delta S\text{chel} = \Delta S\left\{\text{M}(\text{EDTA})\right\} - \Delta S\left\{\text{M}(\text{MIDA})_2\right\} \text{-------------------} (54\text{a})$$

The changes in thermodynamic properties on chelation are listed in table XXIX.

TABLE XXIX

<u>The Chelate Effect Thermodynamic Functions for Reaction</u> (S)

$(\text{MIDA})_2 \rightarrow \text{EDTA}$	$-\Delta G$ (k.cal.mole^{-1})	ΔH (k.cal.mole^{-1})	ΔS (cal.deg^{-1}mole^{-1})
Mg^{2+}	3.65	+1.31	+17.1
Ca^{2+}	5.27	-4.62	+2.7
Zn^{2+}	3.23	+0.98	+14.6
Cd^{2+}	6.87	-1.78	+11.9

It can be seen that in the cases of the Mg^{2+}, Zn^{2+} and Cd^{2+} complexes, chelation is accompanied by a fairly large entropy change and a small change in enthalpy. The endothermic heat changes for Mg^{2+} and Zn^{2+} complexes are due to the greater strain involved in fitting another chelate ring around these small ions. The larger endothermicity for the smaller Mg^{2+} ion emphasises this point. Possible structures for the N-MIDA and EDTA complexes are shown in Figure 21 assuming octahedral symmetry. The chelate effect for these three metals is therefore largely an entropy effect which can be ascribed to the increase in the number of free solute particles accompanying complex formation with a consequent increase in S_g. Some increased ordering of solvent molecules might be expected for the two free ions compared to the single ion but if this is the case the effect is overshadowed by the release of an extra species into the solution.

In contrast to these results, it is seen from table XXIX that the chelate effect for the calcium complexes is principally one of enthalpy. This can be explained by the strain free structure for $Ca(EDTA)^{2-}$ as compared to the complexes involving the smaller cations and it is seen that the cadmium complex also follows this general trend. It is, however, difficult to explain the extremely small increase in entropy.

From the structural point of view there have been no X-ray studies of the alkaline earth aminopolycarboxylate complexes. Using X-ray crystallography, Hoard and co-workers have established the structures of the EDTA complexes of Co(111)[84], Ni(11)[85], Fe(111)[86] and Mn(11)[87]. While these X-ray studies have provided considerable insight into the problem a danger exists in extrapolating these results to aqueous solutions and especially to other systems in solution.

Octahedral symmetry as shown in Figure 21 for complexes of N-MIDA and other EDTA-like ligands with the small magnesium ion imposes a great deal of strain upon the ligand structure. Much of this strain is removed if a tetrahedral structure is envisaged and on the basis of the results obtained so far it is not possible to make a choice between these possibilities. Lind, Lee and Hoard[88] from the results of X-ray studies with lanthanum EDTA complexes have shown that the predominant species is $[La(OH_2)_4EDTA]H$ which has a distorted octahedral structure leaving room for water molecules to be retained on the metal ion. The heat and entropy data presented in the present work suggests that similar structures may exist for the aminocarboxylate complexes of the barium ion which is even larger than La^{3+}.

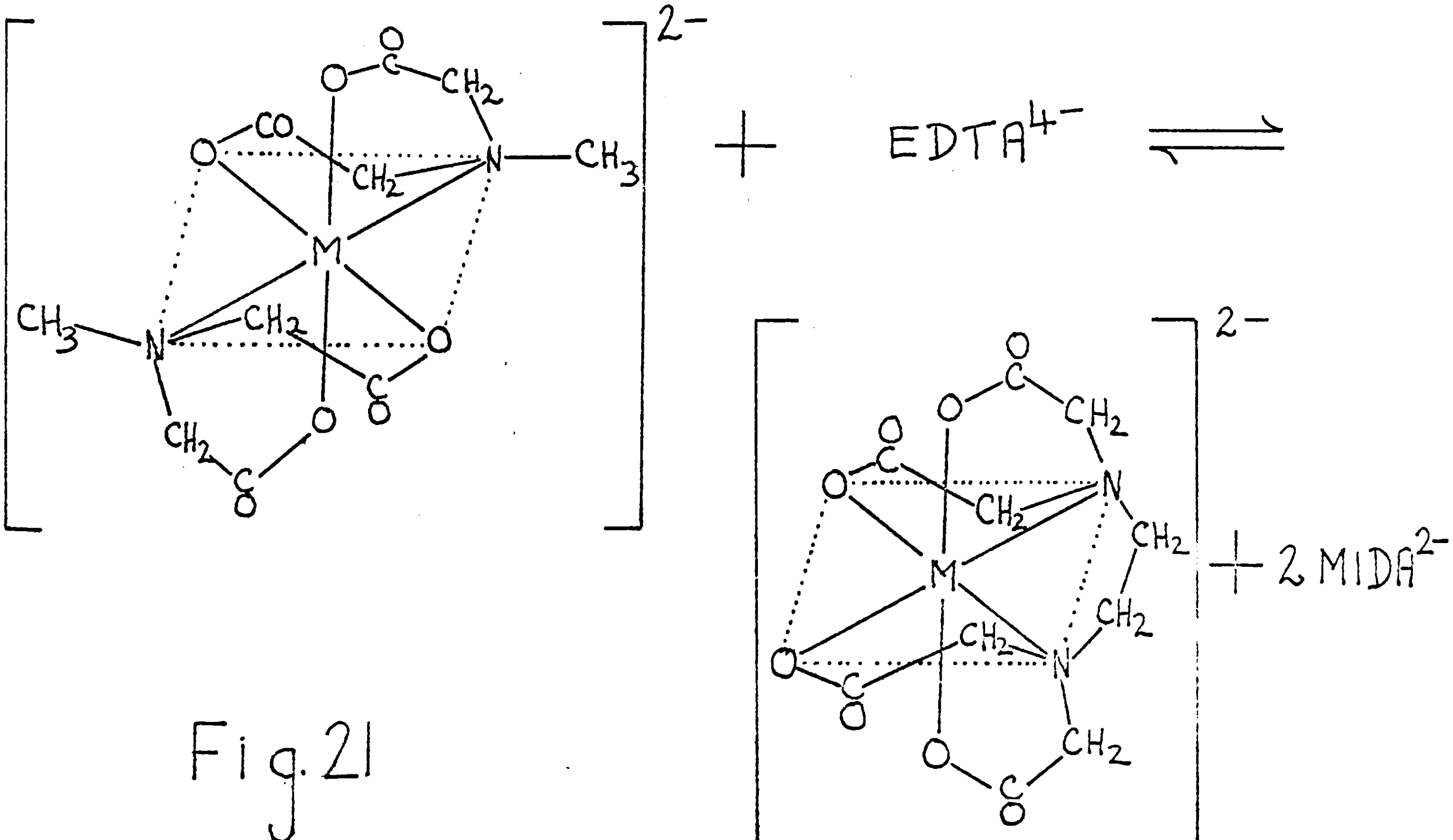


Fig. 21

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