CHAPTER TWO

BINARY METAL-AMINO ACID SYSTEMS

As observed in the previous chapter, various factors govern the stability of a complex. A measure of the stability of a complex in solution is its stability constant. For a complex $[ML_n]$ the stability constant K_n can be represented as follows :

$$M + n.L \rightleftharpoons ML_n \qquad (2.1)$$

$$K_n = \frac{[ML_n]}{[M][L]^n} \qquad (2.2)$$

Jannik Bjerrum was first to introduce the concept that the formation of a complex in solution takes place in steps, each step being governed by a constant termed the stepwise formation constant. For example the complex $[ML_2]$ is formed in two steps :

$$M + L \rightleftharpoons ML_1 \qquad (2.3)$$

$$ML_1 + L \rightleftharpoons ML_2 \qquad (2.4)$$

The first and second stepwise formation constants are represented as follows :

$$K_1 = \frac{[ML_1]}{[M][L]} \qquad (2.5)$$

$$K_2 = \frac{[ML_2]}{[ML_1][L]} \qquad (2.6)$$

and

$$\beta_2 = K_1.K_2 = \frac{[ML_2]}{[M][L]^2} \qquad (2.7)$$

Bjerrum[1] introduced the term $\bar{n}$ which describes the average number of ligands bound per metal ion. For a complex ML_2 the expression for $\bar{n}$ is as follows :

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2} \qquad (2.8)$$

It is presumed that the polynuclear complexes and proton bearing complexes do not existtt in solution.

During complex formation there is competition between protons and the metal ion for the ligand ion. The hydrogen ions also combine with the basic ligand or ligand ion in steps, e.g. the ligand ion, L^{2-} gets protonated in two steps,

$$L^{2-} + H^+ \rightleftharpoons LH^-, \quad LH^- + H^+ \rightleftharpoons LH_2 \qquad (2.9)$$

The equilibrium constants governing each steps are termed first and second proton ligand formation constants, K_1^H and K_2^H.

The function $\bar{n}_H$ can be defined as the average number of protons bound per not complex bound ligand. If the total concentration of ligand is T_L°, and that of metal ion is M, the concentration of free ligand is equal to $T_L^\circ - \bar{n}.M$. The free ligand exists in the solution in the form of undissociated molecule H_2L and the ions HL^- and L^{2-}.

$$T_L^\circ - \bar{n}T_M = H_2L + HL^- + L^{2-} \qquad (3.0)$$

This can be further solved to get the value of pL i.e. negative logarithm of free ligand ion.

$$-\log L = pL = \log \left[\frac{1 + P_{K_1^H}\left(\frac{1}{\text{antilog } B}\right) + P_{K_1^H}.P_{K_2^H}\left(\frac{1}{\text{antilog } B}\right)^2 \frac{V^\circ + V''}{V^\circ}}{T_L^\circ - \bar{n}.T_M^\circ} \right] \qquad (3.1)$$

Bjerrum[2] has shown that values of pL at $\bar{n} = 0.5$ and 1.5 correspond to the metal ligand formation constants $\log K_1$

and $\log K_2$. The values are, however, not very precise. The plots of $\bar{n}$ against pL give the formation curves. Various computations of the $\bar{n}$ and pL values have been attempted to get the precise values of the formation constants. Amongst them the method of least square is supposed to be most precise and has been used in the present study.

Various techniques have been adopted to calculate the values of $\bar{n}$ and pL over the particular pH range. Irving and Rossotti[3] used an extension of Calvin Melchior technique of titration to calculate the values of proton ligand formation constants and metal ligand formation constants, simultaneously.

Amongst the various complexes studied, the amino acid complexes find a very significant position. A large number of papers describing the study of amino acid complexes have appeared and have been reviewed in an earlier thesis from this laboratory.

Ley[4], who investigated the properties of copper glycinate, was the first to recognise the special significance of the cyclic structure of complex compounds. The colour reactions of glycine and alanine with ferric salt were reported by Dubsky and Langer[5]. Polarographic, potentiometric and conductometric studies on the aspartate and alanine complexes of Cu(II) have been reported[6]. The stability constants of metal complexes of a series of α-amino acids were determined by Maley and Mellon[7]. The reactions of Cr(III) with glycine and alanine, resulting in the formation of crystalline products, have been studied[8]. The polarographic behaviours of Zn(II), Co(II) and Ni(II) in glycine solution were studied by Kopanica and Dolezal[9]. The formation constants of Cd(II) complexes with various amino acids have been reported[10]. The stability constants

of twenty 1:1 Fe(II) complexes with α-amino acids have been worked out.[11] Complexes of La(III) and Ce(III) are known to be formed with amino acid ligands[12]. The infra red absorption spectra of many metal alanine complexes have been recorded.[13] complexation of uranyl ion(VI) with amino acids in 1:1 ratio, at pH 1.5, has been inferred by absorption study in the visible range[14]. The infra red spectra of thirty metal chelates of eight amino acids were measured both in aqueous solution and in the crystalline state and the data on relative strengths of the M-O bonds of various metals have been compiled[15]. Cd(II) chelates with alanine and nor-leucine were isolated by Fedrove and Balakneva[16]. Another interesting polarographic behaviour of Cd(II) α-amino acid system has been observed.[17] The first and the second formation constants of the complexes of La(III),Pm(III) and Nd(III) with glycine are known.[18] The proton magnetic resonance spectra of twelve α-amino acid ligands in the presence and absence of Cd(II) and Cu(II) ions were obtained and interpreted.[19] Nature of the metal donor bonds in amino acid chelates has also been investigated by infra red spectral studies.[20] Coordination compounds of uranyl acetate with amino acids have been synthesised and characterised.[21] Potentiometric study at different temperatures yielded the equilibrium constants of serine or alanine and Ag(II) systems.[22] Biswas and coworkers[23] have studied the IR spectra of dehydrated complexes of Cu(II), Ni(II),Zn(II),Co(II) and Pd(II) with glycine, α- and β-alanine in the range 3000-4000 and 1700-1500 cm^{-1} regions. The polarographic behaviour of Cd(II) complexes with amino acids, at various pH, weresstudied by Rao and Subramanya.[24] Scandium salts of glycine, α-alanine

and nor-leucine have also been reported[25]. The stability constants of Ag(I) complexes with some amino acids and the ionisation constants of these acids have also been studied[26]. Curve fitting, correction term and elimination methods were used to calculate the stability constants of Cu(II), Cd(II) complexes with glycine[27]. The temperature jump method was used to determine the complexation and rate constants for the formation of α- and β-alanine complexes with Ni(II) and Co(II)[28]. Different methods have been used by Gergely and Mojges.[29] Recently Chopra and coworkers reported the stability constants of Mn^{2+} and UO_2^{2+} complexes of methionine and leucine by using Irving Rossotti titration technique[30]. Tanner and Choppin[31] utilized the solvent extraction method to characterise the thermodynamic parameters and stability constants of lanthanide and actinide complexes of glycine. Sahu and Bhattacharya[32] have studied the complexes of Tl(I) with the amino acid ligands by conductometric and spectrophotometric methods, while the Tl(III) complex of glycine having composition $Tl(gly)_3Cl_3$ has been prepared and characterised by I.R. spectral studies.[33] The Cu(II) complexes with glycine and alanine have been studied by I.R., DTA and X-ray diffraction methods.[34] The precipitation reactions, bond properties and I.R. spectra of Pt(II)-glycine complexes with ethylene or CO have been reported.[35] Co(III) glycine oxine complex has been prepared and characterised by I.R. and paper chromatographic technique.[36] The I.R. spectra of a series of crystalline α-amino acids and the corresponding bis(amino-acidata)Cu(II) complexes have been investigated[37]. The complexes of leucine with Cu(II), Ni(II),

Zn(II), Co(II) and Cd(II) have been studied[38]. Pierre Britton studied the Cu(II) chelates with the three isomeric forms of leucine[39]. The stability constant of the Cu(II), leucine system was determined potentiometrically[40]. The polarographic behaviour of Zn(II) was studied in the presence of glutamic acid, aspartic acid and valine by Sundersan and Sundaram[41]. Kodama and coworkers[42] have studied the complex formation equilibria of the Pb(II) ion with aspartic acid and IMDA by polarographic method. Huenze and Rudolf[43] studied the complexing constants of Cd with aspartic acid, glutamic acid, glycine, β-alanine and γ-amino butyric acid by potentiometric method at different temperatures. The stability constants of rare earth complexes with aspartic acid were also determined by potentiometric method[44]. The uranyl complexes of dextro and levo aspartic acids have been investigated by polarographic, conductometric and potentiometric methods[45]. The Rh(III) complexes of aspartic acid and glutamic acid have also been reported[46].

It is observed that the amino acid complexes of Ag(I), Cd(II), Zn(II), Ni(II), Be(II) and Cu(II) have not been systematically studied. In the present work the studies of glycine, α-alanine, β-alanine, leucine and iso-leucine complexes of Ag(I) and Cd(II) and aspartic acid complexes of Cd(II), Zn(II), Ni(II) and Be(II) have been carried out.

(A) Experimental :

Irving-Rossotti titration technique[47] was employed for the determination of the proton ligand and metal ligand formation constants in solution. This technique involves the measurement of pH, which was carried out using a glass calomel electrode and pH meter combination. All the ligands, and metals are freely soluble in water and hence water was used as solvent throughout the investigation of these systems.

(a) Materials and purification :

(i) Water : Throughout the experimental work double distilled conductivity water was used. Distilled water was redistilled over alkaline potassium permanganate. The distillate was boiled to expel carbondioxide and was cooled and stored in an air-tight pyrex aspirator. The pH of this water was found to be ~ 6.8. This water was used for preparing solutions of metals and reagents.

(ii) Ligands and other chemicals : The ligands used were A.R. pure. They were obtained from different chemical companies, and their purities were checked by noting the melting points. The chemicals used are listed below :

Glycine (Rienal, pure, Hungary); leucine (E.Merck, A.G.); α-alanine, β-alanine, iso-leucine and aspartic acid (BDH, A.R. pure, biochemicals); glycollic acid and malic acid (Riedel, pure); lactic acid,(May and Baker, pure); perchloric acid (Baker analysed reagent, N.J.); sodium perchlorate (Fluka, pure); sodium hydroxide (S.Merck, A.R.); nickel carbonate (supplied by Canning and Co., Birmingham-18); copper carbonate (E.Merck, G.R.);

cadmium carbonate and zinc carbonate (BDH, A.R.); silver nitrate and beryllium nitrate (BDH, A.R.) were used.

(b) (i) Oxalic acid : Standard oxalic acid solution of strength 0.2M was prepared by dissolving the required amount of the sample (BDH, A.R.) in conductivity water and making upto required volume.

(ii) Sodium hydroxide : 50 gms. of sodium hydroxide was dissolved in 500 ml. conductivity water in a well corked pyrex flask and was kept for two days. The clear supernatant liquid was filtered rapidly through sintered glass crusible of porosity G-4 using vacuum pump into another well cleaned 500 ml. measuring flask. It was then diluted to 500 ml., shaken well and titrated against standard 0.2N oxalic acid solution using phenolphthalein as an indicator. Thus the strength of the sodium hydroxide solution was determined and also checked pH metrically. From this standard sodium hydroxide solution, solution of required normality (0.2M) was prepared by proper dilution. Care was taken to keep the sodium hydroxide solution free from atmospheric carbondioxide.

(iii) Sodium perchlorate solution : 1M solution was prepared by weighing the required weight exactly. It was diluted to obtain solutions of different concentrations.

(iv) Perchloric acid solution : A definite volume of 80 % acid was diluted with conductivity water to obtain 0.5M solution of perchloric acid in 500 ml.. The exact strength was found out by titrating against standard alkali.

(v) Metal salt solution : In order to avoid the complexing tendencies of the anion, the perchlorates of cadmium, nickel and

zinc were prepared by refluxing their respective carbonates with perchloric acid till an excess of metal carbonate was left. The filtrate was a neutral solution of metal perchlorate. In case of the preparation of copper perchlorate, however, weighed quantity of copper carbonate was dissolved in known excess of perchloric acid. This is to avoid the hydrolysis of Cu(II). Silver and beryllium nitrates were used, due to non availability of pure quality of their carbonates, necessary for the preparation of perchlorate. The amounts of metal present were estimated. From this stock solution, 0.01M metal perchlorates were prepared by proper dilution.

(vi) Solutions of complexing agents : Since all the ligands were of A.R. pure quality, their standard solutions of 0.05M concentration were prepared by dissolving the required quantity in conductivity water.

(c) Apparata : All glassware used were pyrex. The micro burette was calibrated to 0.01 by the method described by Vogel[48]. The other measuring vessels as micro pipettes, measuring flasks of various capacities, pipettes etc. were calibrated by using a standard burette.

(d) pH-Meter and accessories : A Metrohm pH meter of type E-350A operating on 220 - 240 volts and 40 - 60 cycles and designed for the entire pH range from 0 to 14 and having glass and calomel electrode combination was used. The pH meter has readability of $\pm$ 0.05 unit and a reproducibility of 0.02 pH unit. It was calibrated with buffer of pH 4 and 7. The calibration was intermittently checked.

(e) Details of Irving-Rossotti titration technique : The titration

cell was a pyrex beaker fitted with a perspex cover with holes through which were admitted the electrode, burette tip and glass stirrer. The tip of the burette was kept in contact with the solution and positioned as near to the stirrer as possible to avoid local concentration of alkali. In all three solutions were prepared (1) perchloric acid, (2) perchloric acid + ligand and (3) perchloric acid + ligand + metal. The total volume of 50 ml. was maintained by the addition of conductivity water and the initial ionic strength of the solution was raised to 0.2M in all the cases by the addition of the required amount of the neutral salt i.e. sodium perchlorate. The three solutions for the titrations were prepared as shown below :

(1) Acid titration :

0.02M $HClO_4$, 0.178M $NaClO_4$

(2) Reagent titration :

0.02M $HClO_4$, 0.01M ligand and 0.178M $NaClO_4$

(3) Metal titration :

0.02M $HClO_4$, 0.01M ligand, 0.001M metal salt solution and 0.169M $NaClO_4$.

The titration beaker containing above solutions were kept for at least 10-25 minutes in the waterbath in order to allow them to attain that temperature (30°C.).

The ratio of the metal salt to ligand was maintained at 1:10 in all the metal titrations so as to satisfy the highest possible coordination number of the metal ions studied. After the addition of each portion of alkali, pH was noted. The highest reading which remains steady was recorded in all the cases. The titration data and curves are given in tables

II 1.1 to II 1.7 and in figures II 1 to II 7.

(B) Determination of proton ligand and metal ligand stability constants :

As seen in the Irving-Rossotti titration curves (fig. II 1 to II 7) for the same volume of alkali, the ligand formation curve is positioned in two different ways, with respect to the acid curve in the two different regions of pH. At low pH the ligand titration curve shows higher values of pH than the acid titration curve indicating that it contains less number of titratable hydrogen ions. This is due to the formation of the species $R.NH_3^+.COOH$. At higher pH it exhibits lower value of pH than the acid titration curve showing more number of titratable hydrogen ions due to dissociation of COOH group. From the displacement of these two curves $\bar{n}_H$ values can be calculated.

The association of proton with amino acid takes place in the two stages.

$$NH_2.R.COO^- + H^+ \underset{\text{pH 7.0 to 9.0}}{\overset{K_1^H}{\rightleftharpoons}} NH_3^+.R.COO^-$$

$$NH_3^+.R.COO^- + H^+ \underset{\text{pH 2.0 to 5.0}}{\overset{K_2^H}{\rightleftharpoons}} NH_3^+.R.COOH$$

Further the metal complex is formed by reaction of the type $M^{2+} + LH \rightleftharpoons ML^{+} + H^{+}$. Thus the ligand on coordination with metal releases extra H^{+} ions in solution and hence the metal + ligand solution contains still more titratable hydrogen ions. The metal titration curve, therefore, shows lower pH value for the same amount of alkali than the ligand titration curve. Thus $\bar{n}$ factor can be computed from the difference in the volume of alkali required to produce the same pH in the metal + ligand and ligand titrations. To put in other words the displacement of the metal + ligand curve has to be measured with respect to the ligand curve along the volume axis of a "pH versus volume of alkali plot".

(i) Calculation of $\bar{n}_H$ and proton ligand stability constants :

The $\bar{n}_H$ value can be calculated by using curves first and second. The horizontal difference between these two curves is used for the calculation of $\bar{n}_H$ at different pH by using following equation :

$$\bar{n}_H = \frac{(V'-V'')(N + E^\circ)}{(V^\circ + V').T_L^\circ} + Y \qquad (3.2)$$

where,

$\bar{n}_H$ = Mean number of protons bound per not complex bound ligand molecule.

V° = The initial volume of solutions.

V', V'' = Volumes of alkali required to attain the same pH in the acid and acid + ligand curves.

N = The concentration of alkali.

E° = The initial concentration of mineral acid

T_L° = The initial total ligand concentration.

Y = Number of replacable hydrogens from ligand.

The values of proton ligand stability constants have been obtained by linear plot of pH against log $\bar{n}_H/1-\bar{n}_H$. At each point on the straight line pH - log $\bar{n}_H/1-\bar{n}_H = K^H$. K_1^H and K_2^H values were obtained in the range $\bar{n}_H$ 0 to 1 and 1 to 2 respectively, and have been represented in table II 4.0. The details of intermediate stages of calculations and graphs have not been given because such data have been incorporated in the thesis submitted earlier.[49] However, the calculations had to be repeated to get K^H values under same experimental conditions.

(ii) Calculation of metal ligand formation constants :

The $\bar{n}$ values have been calculated by measuring horizontal difference in volume of alkali required to produce the same pH in the metal and ligand titration and substituting it in the following equation :

$$\bar{n} = \frac{\left[(V''-V'')\left\{N + E^\circ + T_L^\circ\,(Y - \bar{n}_H)\right\}\right]}{(V^\circ + V'').\bar{n}_H.T_M^\circ} \qquad (3.3)$$

where

T_M° = Initial total metal ion concentration.

V'', V'' = Volumes of alkali required to attain the same pH in the acid + ligand and metal curves.

(iii) Calculation of pL :

For the calculation of pL, the equation (3.1) was used. The pL values calculated have been recorded in tables II 2.1a to II 2.6a, II 2.1b to II 2.5b and II 2.6c to II 2.6e. The values of $\bar{n}$ have an accuracy of $\pm$ 0.01 depending on the burette precision and the values of pL are significant upto $\pm$ 0.05

depending upon the readability of the pH scale.

Values of $\bar{n}$ obtained can be plotted against pL to get the metal ligand formation curves and log K_1 and log K_2 can be calculated from pL values at $\bar{n} = 0.5$ and 1.5, respectively. The formation curves in all the cases have been presented in figures II 8 to II 21. However, this graphical method makes use of only one point for the determination of stepwise formation constants and may introduce experimental error. Further, the formation curves do not show flattening at $\bar{n} = 1$ indicating that the spreading factor in the formation of the first and second step of formation of metal ligand complexes is not high. The values of log K_1 and log K_2 obtained by direct interplotation at half $\bar{n}$ values are, therefore, very approximate. Unless log $K_1 / K_2 > 10^{2.5}$, the above commonly used approximation can introduce considerable error, and hence has not been used for the calculation of formation constants. The values have been obtained by using the method of least square, as follows :

It is seen from equation (2.8) that the above approximate method need not be used, if N equation, of the type referred in equation (2.8), are available for the system with MA_N as the highest possible complex. The experimental data, however, exceed the minimum requirment and problem faced is to choose the most representative values. It is observed that the values of $\bar{n}$ near an integer value must be used very cautiously since the $(\bar{n} - 1)$ is very susceptible to small error. This raises the question of choice of suitable values of $\bar{n}$ and pL. Different workers have adopted different methods suitable to their experimental

conditions. Irving and Rossotti[3] and Hearon and Gilbert[50] have summarised the uses of these methods in their reviews. The least square treatment of $\bar{n}$ and pL data gives the most representative values of K_1 as suggested by Irving and Rossotti[3]. The same method has been used in the present investigation and is being summed up as follows. In the cases of systems with ML_2 as the highest complex,

$$\bar{n} + (\bar{n}-1)\, K_1[L] + (\bar{n}-2)\, K_1.K_2 [L]^2 = 0 \qquad (3.4)$$

The above equation may be rearranged as follows :

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})\,[L]}{(\bar{n}-1)} \cdot \beta_2 - K_1 \qquad (3.5)$$

The above equation is well known for a straight line of which the slope is β_2 ($K_1.K_2$) but, since the term $[L]$ varies over several powers of ten, it is difficult to plot

$$\frac{\bar{n}}{(\bar{n}-1)[L]} \quad \text{vs} \quad \frac{(2-\bar{n})\,[L]}{(\bar{n}-1)}$$

Therefore, the constants β_2 ($K_1.K_2$) and K_1 are best evaluated by the method of least square, It makes use of all the experimental points except those between $\bar{n}$ = 0.95 and 1.05 (which, for this purpose, are too sensitive to slight experimental errors). In this method firstly the values of $\bar{n}/(\bar{n}-1)[L]$ and $(2-\bar{n})[L]/(\bar{n}-1)$ were calculated, these values are termed y and x and were summated over all number of points taken to give Σy and Σx, respectively. Next, values of x^2 and xy, were tabluated and added to give Σx^2 and Σxy, respectively. These sums were used to solve the standard simultaneous equations for the least square which are

$$\sum y = K.ao + a_1 \sum x$$

$$\sum xy = ao \sum x + a_1 \sum x^2 \qquad (3.6)$$

where K is equal to the number of observations, the coefficient ao is $-K_1$ and a_1 is β_2. The solution of equation (3.6) gave mean value for log K_2. Further, the mean value of K_1 was fitted into equation (3.5) and then individual values from the average value were determined. From the sum of individual deviation the average of these deviations, i.e. mean deviation, was calculated. The calculations and precise values of first and second formation constants obtained by this method have been tabulated in tables II 3.1a to II 3.6a, II3.1b tp II 3.5b and II 3.6c to II 3.6e.

In cases of Ag(I) and Cd(II) β-alanine systems the $\bar{n}$ values do not go beyond one and least square calculations yielded negative values of β_2 ($K_1.K_2$) indicating that the second step of formation does not start in this range.

In such cases, another method was adopted to improve the values of log K_1 obtained from pL at $\bar{n} = 0.5$. The formation function in case of 1:1 complexes can be expressed as,

$$\bar{n} + \log K_1 (\bar{n} - 1) = 0 \qquad (3.7)$$

it can be rearranged as

$$\log (1-\bar{n})/\bar{n} = pL - \log K_1 \qquad (3.8)$$

This, in other words, means that log $(1-\bar{n})/\bar{n}$ shows a linear function with pL. Plots of log $(1-\bar{n})/\bar{n}$ versus pL give linear graphs as shown in figs. II 16 and II 17. The values of log K_1 can be calculated at each point on the straight line by using the following relationship[51]:

$$\log K_1 = pL - \log(1-\bar{n})/\bar{n} \qquad (3.9)$$

The values of log K_1 at different pH have been presented in tables II 3.3a and II 3.3b. The average of all these values was obtained and the deviation of each individual value from the average value was calculated.

The method, described above, has following advantages : (i) The values of log K_1 is not obtained only from one point ($\bar{n} = 0.5$) and the possibility of experimental error is eliminated. (ii) The points on the straight line are considered and thus the validity of $\bar{n}$ and pL values can be verified. The most divergent points away from the linear relationship can be discarded.

The average values of log K_1 and log K_2 with mean deviation obtained by least square or linear plot method, have been represented in table II 5.1.

In case of Cu(II) aspartate complex $\bar{n}$ values lower than one are obtained in the region where the curves are horizontal. As such precise calculation of $\bar{n}$ is not possible.

It is observed that the proton ligand stability constant values of amino acids are in the order :

β-alanine > α-alanine > Glycine > Leucine ≈ iso-leucine.

This order is valid for both the first and second proton ligand formation constants. As studied earlier (page No. 96) the first constant corresponds to the association of protons with $NH_2.R.COO^-$ and the second constant governs the combination of proton with $NH_3^+.R.COO^-$. The theoretical explanation for the above order of the formation constants has been discussed earlier[52,53]. The NH_2 group in α-alanine is more basic than in glycine because the addition of methyl group produces

positive inductive and hyper conjugation effects. The effects are, however, not very significant and hance the values of K^H do not differ significantly. The second formation constants for all the ligands are same because the effect of the R- group over COO group may be negligible. In case of β-alanine both $^{P}K_1^H$ and $^{P}K_2^H$ have higher values. This is because the NH_3^+ and COOH groups are at β- position with respect to each other and hence the negative inductive effect of the NH_3^+ over COOH group is less and hence COOH proton becomes less mobile or in other words COO^- has greater tendency to combine with the protons. Similarly the effect of carboxylate over NH_3^+ is also less, resulting in higher value of $^{P}K_1^H$.

It is interesting to compare the values of metal ligand formation constants in case of Cd(II) complexes, The order is as follows :

Glycine $\simeq$ α-alanine $>$ β-alanine $<$ Leucine $\simeq$ iso-leucine

The values of the proton ligand stability of glycine and α-alanine do not differ significantly and hence their basicities are nearly same. It can naturally be expected that their tendencies to form complexes should also be same. Leucine and iso-leucine, though closer in basicity to glycine and alanine, have lower values of M-L formation constants. In all these cases NH_2 group is present at the α- position and hence five membered rings are formed. However, in cases of leucine and iso-leucine bulky groups are linked with the α- carbon atom and make the chelate less stable. This may be because of the steric hindrance or because the chain experiences more

strain on bending when bulky groups are attached to the α- carbon atom.

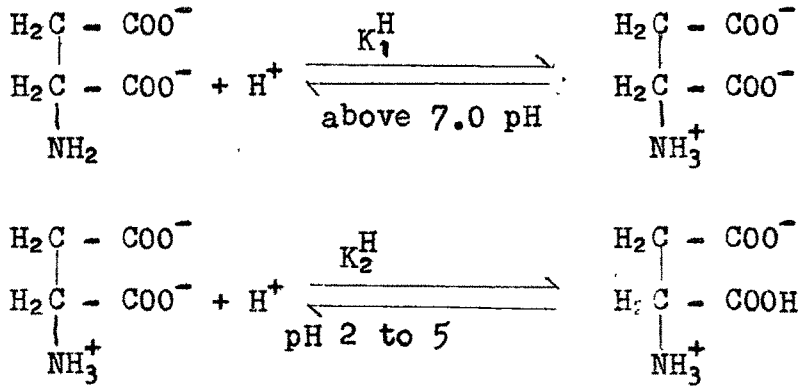
In case of β-alanine the first proton ligand stability constant is higher indicating that the ligand is more basic. However, it forms less stable complex than glycine or α-alanine. It is also not possible to determine the second metal ligand formation constants in case of β-alanine complex of Cd(II). This is because β-alanine has NH_3 group at the β- position and results in the formation of six membered chelate ring. The six membered saturated rings are known to have more strain and hence are less stable. This accounts for the lesser stability of Cd(II).β-alanine complex.

In Ag(I) complexes the order of the stability in case of glycine, α-alanine, leucine and iso-leucine is same as in Cd(II) complexes, and this can be explained as above. The Ag(I) complexes are less stable than the Cd(II) complexes. One of the reasons for this is that Cd(II) has two positive charges, whereas silver ion has only one. Thus the electron attracting capacity of Cd(II) is more. Another factor is the steric condition in Ag(I) complexes. Ag(I) can undergo sp hybridisation resulting in formation of two coordinate complexes with a ligand disposed linearly. The very well known example is $[Ag(NH_3)_2]^+$ complex ion. It can also exhibit coordination number four resulting in square planar or tetrahedral structures. Thus the bidentate ligand in 1:1 complex has to span more to occupy the two coordination positions at an angle of 180° . This brings a significant strain on the ligand resulting in lower values of the formation constants.

The above fact also explains the lower values of the ratio of log K_1 / log K_2 in case of Ag(I) complexes. Though the ligand is strained in 1:1 complex but the two ligands occupy cis positions in the square plane in 1:2 complex. Thus the second ligand experiences much less strain and hence log K_2 has a higher value.

It is also interesting to observe that β-alanine forms more stable Ag(I) complex than glycine or α-alanine. The situation is reverse of what has been observed in case of Cd(II) and other metal ions. The six membered saturated ring should normally be less stable. In case of Ag(I) complex, however, a ligand with longer chain length is favoured because it has to occupy two positions at an angle of 180°. A molecule with a longer chain length will realise less strain. This explains why in case of Ag(I), β-alanine forms more stable complexes than glycine. Similar observations have been made in case of Ag(I) complexes of diamines.[54] The amines with longer chain lengths are known to form more stable Ag(I) complexes.

In case of aspartic acid the stages of protonation can be represented as follows :



$$\begin{array}{l} H_2C - COO^- \\ | \\ HC - COOH \\ | \\ NH_3^+ \end{array} + H^+ \underset{\text{below 2 pH}}{\overset{K_3^H}{\rightleftharpoons}} \begin{array}{l} HC - COOH \\ | \\ HC - COOH \\ | \\ NH_3^+ \end{array}$$

Thus it is observed that one of the carboxylate group loses hydrogen at very low pH and hence the formation constant corresponding to the association of H^+ with that COO^- ($^PK_3^H$), could not be calculated. The values of $^PK_2^H$ and $^PK_3^H$ correspond to the formation constants for the combination of H^+ with second COO^- and the NH_2 group. Since the first carboxylic acid gets dissociated below the pH range of metal complex formation, only $^PK_2^H$ and $^PK_3^H$ affect the value of metal ligand formation constant. $^PK_2^H$ and $^PK_3^H$, therefore, correspond to $^PK_1^H$ and $^PK_2^H$ of the mono basic amino acids studied earlier. The value of $^PK_3^H$ of aspartic acid is almost same as that of $^PK_2^H$ for glycine. $^PK_2^H$ value of aspartic acid is, however, slightly higher than the $^PK_1^H$ of glycine. This can be explained to be due to the fact that aspartic acid has an already dissociated carboxylate ion. This will produce positive inductive effect and lower down the dissociation of second COOH. Thus the effective basicity of aspartate ion is more than glycine and hence forms more stable complexes with the metal ion. Further, construction of model shows that the aspartic acid can act as a tridentate ligand, coordination taking place from two COO^- and one NH_2 group. This may be an additional factor for the greater stability of aspartic acid complexes.

The order of the formation constants with different metal ions is as follows :

$$Cu > Be > Ni > Zn > Cd$$

This is in accordance with the extended form of Irving-William order[55]. The factors mainly responsible for the stability of σ-bonding complexes are, ionic potential of the metal ion and the availability of the d-orbitals in it. Be(II) is a non-transition metal ion and hence has no d-orbitals. However, it forms quite stable amino acids complexes because it has a small ionic size and hence covalent interaction in the Be-N bond can be expected to be high. This makes Be-N bond strong.

The order Cu > Ni > Zn for the formation constants of amino acid complexes is in agreement with earlier observations. If the M-L bond is purely ionic in nature, the enthalpy changes during the formation of these complexes should be in the order Zn > Cu > Ni i.e. in accordance with the second ionisation potential of metal ions. However, the formation of the amino acid complexes also results in the liberation of crystal field stabilization energy, which is in undistorted complexes will be in the order $d^8 > d^9 > d^{10}$. This extra stabilization renders the amino acid complexes of Ni(II) more stable than Zn(II) complexes. The greater stability of Cu(II) complexes is due to Jahn-Teller[56] effect which makes the complex distorted and more stable.

The hydroxy analogues of glycine, α-alanine and aspartic acid are glycollic, lactic and malic acids, respectively.

The hydroxy acid complexes of Be(II), Ni(II) and Zn(II) have been studied earlier and the values of the formation constants have been reported.[57-60] The formation constants of Cu(II) complexes of glycollic, lactic and malic acids were

determined by using Irving-Rossotti[47] titration technique. The details are similar to those in case of amino acid complexes and hence only the final values of the formation constants have been presented in table II 5.2. The study of Ag(I) and Cd(II) hydroxy acids complexes was not possible because the complex formation takes place at higher pH, in the range of hydrolysis. This, however, indicates that the complexes are less stable.

It is interesting to compare the formation constants of the amino acid complexes and corresponding hydroxy acid complexes. It is observed that in case of Ni(II), Cu(II), Zn(II), Ag(I) and Cd(II) complexes the amino acids are more complexing than corresponding hydroxy acids, indicating thereby that M-N > M-O. This is in agreement with the expected type III (page No. 3) behaviour of these metal ions. The order can be explained in terms of electronegativity of nitrogen and oxygen, the repulsion between the d-orbitals of metal ions and two lone pairs on oxygen atom and also the higher crystal field splitting brought about by the amino acids. This has been discussed in detail earlier (page No. 5). In case of Be(II) the values of formation constants for the amino acid complexes are lower than the corresponding hydroxy acid complexes, indicating thereby that M-O > M-N. Thus Be(II) exhibits type (I) behaviour. According to earlier classification Be(II) should exhibit class II behaviour i.e. Be-O should be equal to be Be-N. This can be explained by considering that the above classification of metal ions in type I, II and III is rigidly valid in case of structurally related ligands.

The classification does not universally hold good and various deviations have been observed earlier. However, in the present study the oxygen atom in hydroxy group is associated with only one hydrogen, whereas the nitrogen in the amino group is attached to two hydrogens. Further, during complexation the -OH group loses H^+ ion resulting in charged O^- ion. Thus the total charge on the complex ion will be different in the hydroxy acid and the corresponding amino acid complexes, resulting in different entropy changes. It is observed that log K_2 values of the amino and hydroxy acid complexes of Be(II) have lesser difference. This can also be explained in terms of charges. The ligand ions in case of hydroxy acid complexes have two negative charges whereas amino acid ion has only one negative charge. Thus when the second ligand ion gets associated with ML it feels less repulsion in case of amino acid complexes than in case of hydroxy acid complexes resulting in smaller separation between log K_1 and log K_2 in case of amino acid complexes.

In the earlier publications[57-60] from this laboratory comparative study of the formation constants of hydroxy and corresponding mercapto acid complexes have also been carried out and metals have been classified into class A and class B depending on the stability of M-O and M-S bonds. However, the reason for the greater stability of M-S bond is still not clear, as discussed in the previous chapter. In order to throw some light on the nature of M-S bond, studies in ternary systems have been carried out in the later chapter.

Table II 1.1

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.02M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		Glycine		Ag(I)		Cd(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.65	1.00	1.80	1.00	1.80	1.00	1.80
2.00	1.80	2.00	2.05	2.00	2.05	2.00	2.05
2.50	1.85	2.80	2.25	2.80	2.25	2.80	2.25
3.00	2.00	3.00	2.30	3.00	2.30	3.00	2.30
3.60	2.10	3.40	2.45	3.40	2.45	3.40	2.45
3.80	2.20	3.80	2.65	3.80	2.65	3.80	2.65
4.00	2.25	4.00	2.75	4.00	2.75	4.00	2.75
4.20	2.35	4.40	3.00	4.40	3.00	4.40	3.00
4.40	2.50	4.60	3.25	4.60	3.25	4.60	3.25
4.60	2.70	4.70	3.45	4.70	3.45	4.70	3.45
4.70	2.85	4.80	3.65	4.80	3.65	4.80	3.65
4.80	3.10	4.90	4.25	4.90	4.25	4.90	4.25
4.90	3.65	4.92	4.75	4.92	4.75	4.92	4.75
4.94	5.25	4.94	5.30	4.94	5.30	4.94	5.30
4.96	5.75	5.00	7.60	5.00	6.90	4.96	6.20
5.00	8.30	5.04	8.00	5.04	7.20	5.00	6.30
5.02	9.00	5.08	8.20	5.08	7.50	5.04	6.70
5.04	9.45	5.14	8.35	5.12	7.70	5.08	7.00
5.06	9.70	5.20	8.50	5.20	7.95	5.14	7.25
5.08	9.85	5.30	8.70	5.30	8.20	5.20	7.50
5.10	10.00	5.40	8.85	5.40	8.30	5.28	7.75
		5.60	9.05	5.50	8.45	5.36	7.95
		5.70	9.15	5.60	8.60	5.40	8.00
		5.90	9.30	5.70	8.75	5.48	8.20
		6.00	9.40	5.90	9.00	5.60	8.45
		6.20	9.55	6.00	9.05	5.80	8.70
		6.40	9.65		(ppts.)	5.90	8.90
		6.60	9.75			6.00	9.00
		6.80	9.90			6.40	9.45
		7.00	10.00			6.80	9.70
						7.20	10.00

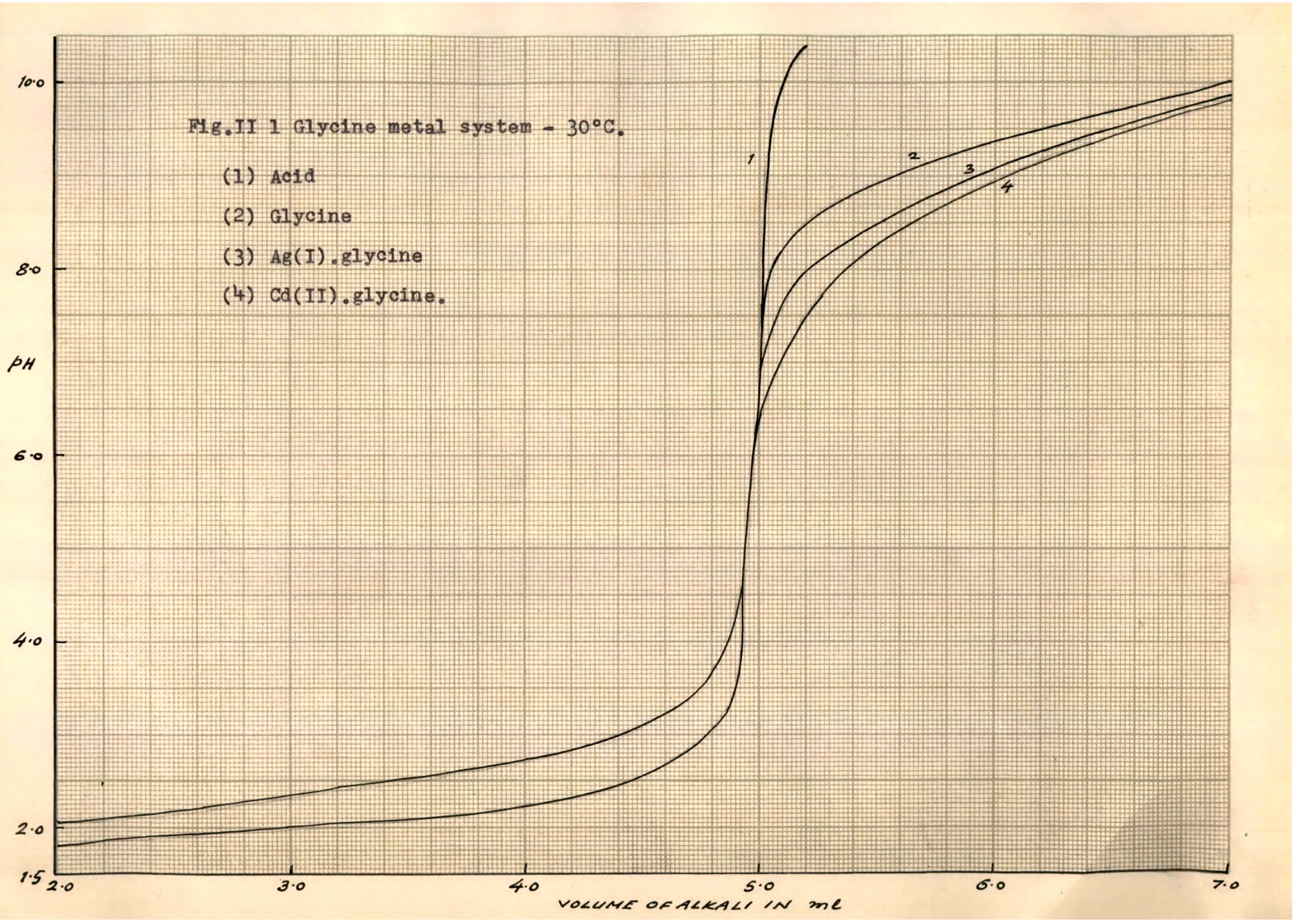


Fig.II 1 Glycine metal system - 30°C.
(1) Acid
(2) Glycine
(3) Ag(I).glycine
(4) Cd(II).glycine.
1
2
3
4
10·0
8·0
6·0
4·0
2·0
1·5
pH
2·0
3·0
4·0
5·0
6·0
7·0
VOLUME OF ALKALI IN ml

Table II 1.2

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.02M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		α-Alanine		Ag(I)		Cd(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.65	1.00	1.85	1.00	1.85	1.00	1.85
2.00	1.80	2.00	2.05	2.00	2.05	2.00	2.05
2.50	1.85	3.00	2.25	3.00	2.25	3.00	2.25
3.00	2.00	3.60	2.50	3.60	2.50	3.60	2.50
3.60	2.10	4.00	2.70	4.00	2.70	4.00	2.70
4.00	2.25	4.40	2.95	4.40	2.95	4.40	2.95
4.20	2.35	4.60	3.20	4.60	3.20	4.60	3.20
4.40	2.50	4.80	3.60	4.80	3.60	4.80	3.60
4.60	2.70	4.90	4.20	4.90	4.20	4.90	4.20
4.70	2.85	4.96	5.00	5.00	6.40	5.00	6.05
4.80	3.10	4.98	6.95	5.04	7.00	5.02	6.50
4.90	3.65	5.00	7.45	5.08	7.30	5.06	7.00
4.94	5.25	5.06	8.00	5.10	7.50	5.10	7.20
4.96	5.75	5.10	8.25	5.20	7.80	5.20	7.70
5.00	8.30	5.18	8.50	5.28	8.00	5.30	8.00
5.02	9.00	5.26	8.70	5.40	8.25	5.40	8.20
5.04	9.45	5.40	8.90	5.50	8.45	5.55	8.40
5.06	9.70	5.60	9.10	5.60	8.60	5.60	8.55
5.08	9.85	5.80	9.30	5.70	8.70	5.80	8.85
5.10	10.00	5.95	9.35	5.90	9.00	6.00	9.10
		6.00	9.40	6.00	9.10	6.20	9.25
		6.20	9.55	6.20	9.30	6.40	9.40
		6.40	9.70	6.40	9.50	6.60	9.65
		6.60	9.80	6.60	9.65	7.00	10.00
		6.80	9.95	6.80	9.80		
		7.00	10.05	7.00	10.00		

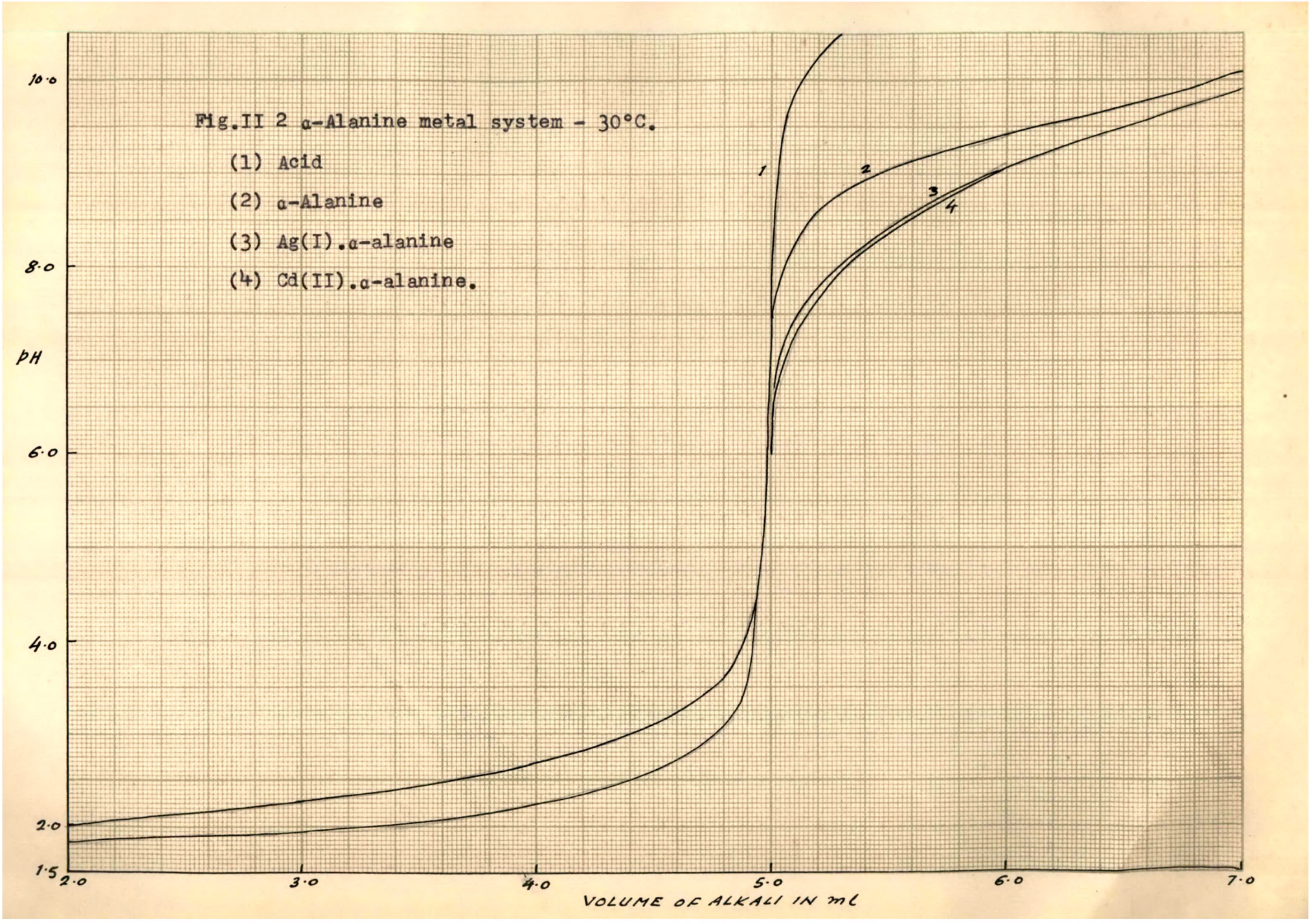


Fig.II 2 α-Alanine metal system - 30°C.
(1) Acid
(2) α-Alanine
(3) Ag(I).α-alanine
(4) Cd(II).α-alanine.
1
2
3
4
10·0
8·0
6·0
4·0
2·0
1·5
pH
2·0
3·0
4·0
5·0
6·0
7·0
VOLUME OF ALKALI IN ml

Table II 1.3

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.02M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		β-Alanine		Ag(I)		Cd(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.65	1.00	2.00	1.00	2.00	1.00	2.00
2.00	1.80	2.00	2.35	2.00	2.35	2.00	2.35
2.50	1.85	2.40	2.60	2.40	2.60	2.40	2.60
3.00	2.00	2.80	2.90	2.80	2.90	2.80	2.90
3.60	2.10	3.00	3.00	3.00	3.00	3.00	3.00
3.80	2.20	3.40	3.30	3.40	3.30	3.40	3.30
4.00	2.25	3.80	3.55	3.80	3.55	3.80	3.55
4.20	2.30	4.00	3.70	4.00	3.70	4.00	3.70
4.40	2.50	4.40	4.00	4.40	4.00	4.60	4.25
4.60	2.70	4.60	4.25	4.60	4.25	4.80	4.70
4.70	2.85	4.80	4.70	4.80	4.70	4.90	5.15
4.80	3.10	4.90	5.15	4.90	5.15	4.95	5.75
4.90	3.65	4.95	5.75	4.95	5.75	5.00	6.75
4.94	5.25	5.00	7.50	5.00	6.75	5.05	7.50
4.96	5.75	5.05	8.30	5.05	7.45	5.08	7.80
5.00	8.30	5.10	8.60	5.10	7.75	5.12	8.05
5.02	9.00	5.15	8.80	5.14	7.90	5.16	8.25
5.04	9.45	5.20	8.90	5.18	8.00	5.20	8.40
5.06	9.70	5.30	9.10	5.20	8.15	5.25	8.50
5.08	9.85	5.40	9.25	5.30	8.40	5.30	8.60
5.10	10.00	5.60	9.50	5.40	8.60	5.40	8.75
		5.80	9.65	5.60	8.90		(ppts.)
		6.00	9.80	5.80	9.20		
		6.20	9.95	6.00	9.50		
		6.30	10.00	6.20	9.70		
				6.40	9.90		
				6.54	10.00		

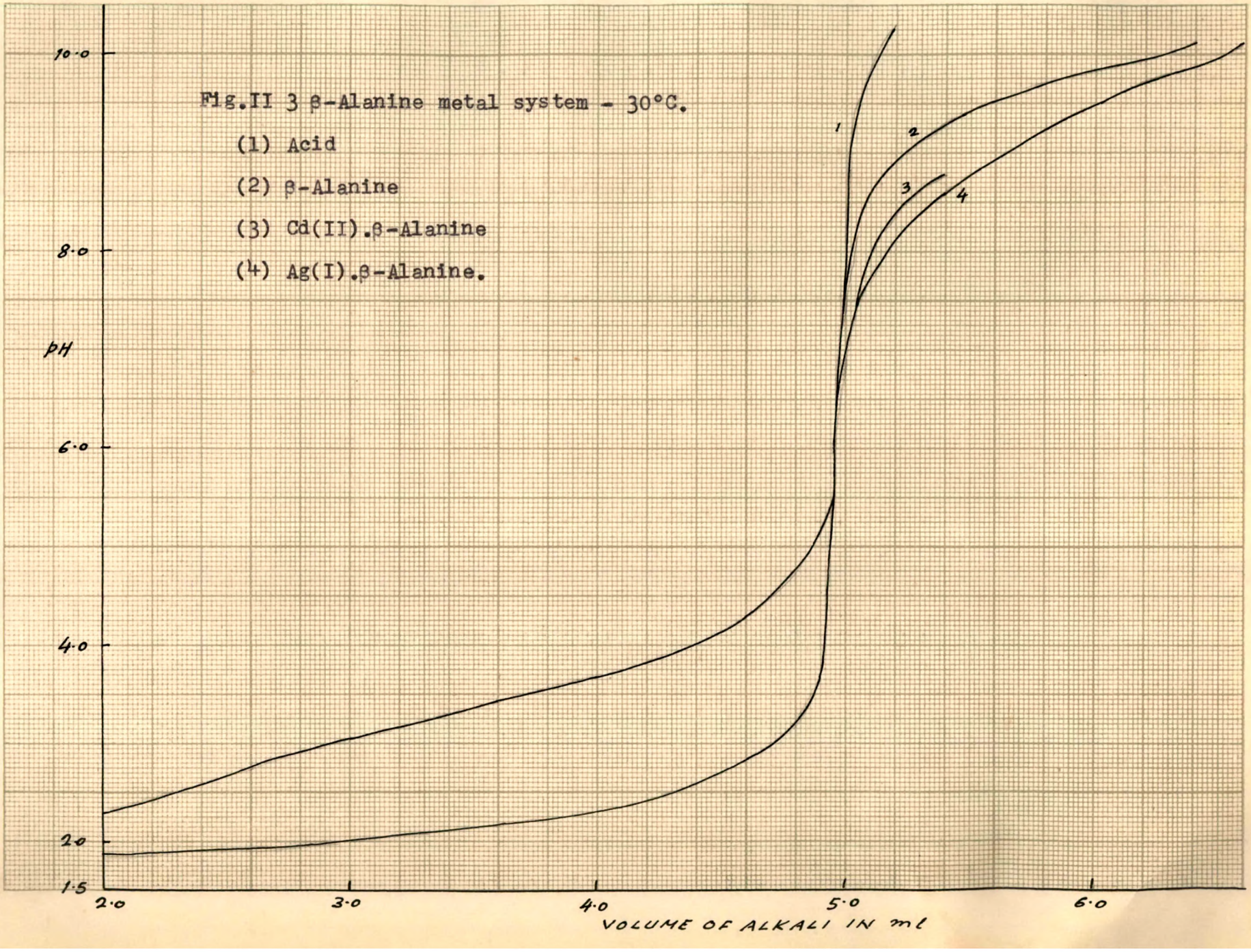


Fig.II 3 β-Alanine metal system - 30°C.
(1) Acid
(2) β-Alanine
(3) Cd(II).β-Alanine
(4) Ag(I).β-Alanine.
10·0
8·0
6·0
4·0
2·0
1·5
pH
2·0
3·0
4·0
5·0
6·0
VOLUME OF ALKALI IN ml
1
2
3
4

Table II 1.4

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.02M T°_{L} = 0.01M T°_{M} = 0.001M

Perchloric acid		Leucine		Ag(I)		Cd(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.65	1.00	1.95	1.00	1.95	1.00	1.95
2.00	1.80	2.00	2.10	2.00	2.10	2.00	2.10
2.50	1.85	2.40	2.20	2.40	2.20	2.40	2.20
3.00	2.00	2.80	2.30	2.80	2.30	2.80	2.30
3.60	2.10	3.00	2.40	3.00	2.40	3.00	2.40
3.80	2.20	3.50	2.55	3.50	2.55	3.50	2.55
4.00	2.25	4.00	2.75	4.00	2.75	4.00	2.75
4.20	2.35	4.20	2.90	4.20	2.90	4.20	2.90
4.40	2.50	4.40	3.05	4.40	3.05	4.40	3.05
4.60	2.70	4.60	3.25	4.60	3.25	4.60	3.25
4.70	2.85	4.70	3.40	4.70	3.40	4.70	3.40
4.80	3.10	4.80	3.65	4.80	3.65	4.80	3.65
4.90	3.65	4.85	3.85	4.85	3.85	4.90	4.20
4.94	5.25	4.90	4.20	4.90	4.20	4.94	5.00
4.96	5.75	4.94	5.00	4.94	5.00	5.00	6.45
5.00	8.30	4.98	6.25	5.00	6.75	5.04	7.00
5.02	9.00	5.00	7.05	5.02	7.00	5.08	7.25
5.04	9.45	5.04	7.80	5.08	7.40	5.12	7.45
5.06	9.70	5.08	8.10	5.12	7.55	5.20	7.70
5.08	9.85	5.12	8.25	5.16	7.70	5.25	7.85
5.10	10.00	5.16	8.40	5.20	7.80	5.30	8.00
		5.20	8.50	5.30	8.05	5.40	8.20
		5.30	8.70	5.40	8.25	5.60	8.55
		5.40	8.85	5.50	8.40	5.80	8.75
		5.60	9.10	5.80	8.80	6.00	9.00
		5.80	9.25	6.00	9.05	6.20	9.20
		6.00	9.45	6.20	9.25	6.40	9.35
		6.20	9.55	6.40	9.40	6.80	9.65
		6.40	9.65	6.80	9.75	7.00	9.80
		6.80	9.90	7.00	9.90		
		6.92	10.00				

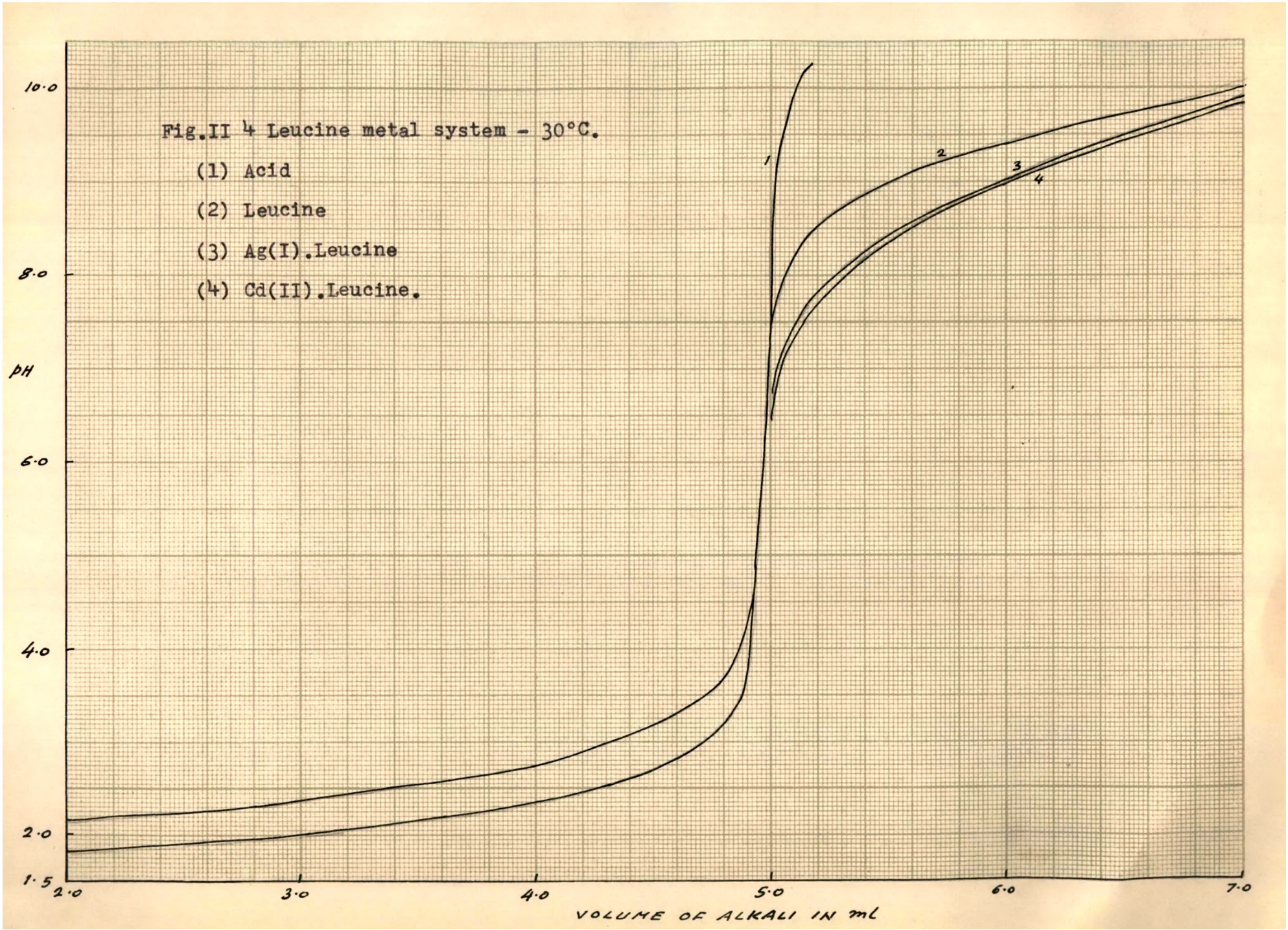


Fig.II 4 Leucine metal system - 30°C.
(1) Acid
(2) Leucine
(3) Ag(I).Leucine
(4) Cd(II).Leucine.
10·0
8·0
6·0
4·0
2·0
1·5
pH
2·0
3·0
4·0
5·0
6·0
7·0
VOLUME OF ALKALI IN ml
1
2
3
4

Table II 1.5

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.2M T_L° = 0.01M T_M° = 0.001M

Perchloric acid		iso-Leucine		Ag(I)		Cd(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.65	1.00	1.95	1.00	1.95	1.00	1.95
2.00	1.80	2.00	2.10	2.00	2.10	2.00	2.10
2.50	1.85	3.00	2.40	3.00	2.40	3.00	2.40
3.00	2.00	3.40	2.55	3.40	2.55	3.40	2.55
3.60	2.10	3.80	2.70	3.80	2.70	3.80	2.70
3.80	2.20	4.00	2.80	4.00	2.80	4.00	2.80
4.00	2.25	4.20	2.90	4.20	2.90	4.20	2.90
4.20	2.35	4.40	3.05	4.40	3.05	4.40	3.05
4.40	2.50	4.60	3.30	4.60	3.30	4.60	3.30
4.60	2.70	4.70	3.50	4.70	3.50	4.70	3.50
4.70	2.85	4.80	3.80	4.80	3.80	4.80	3.80
4.80	3.10	4.85	4.05	4.85	4.05	4.85	4.05
4.90	3.65	4.90	4.60	4.90	4.60	4.90	4.60
4.94	5.25	4.95	5.50	5.00	6.20	4.95	5.40
4.96	5.75	5.00	7.40	5.04	6.80	5.00	6.30
5.00	8.30	5.04	7.90	5.08	7.25	5.04	6.80
5.02	9.00	5.08	8.15	5.10	7.40	5.08	7.20
5.04	9.45	5.12	8.25	5.14	7.70	5.12	7.40
5.06	9.70	5.16	8.40	5.18	7.80	5.16	7.60
5.08	9.85	5.20	8.55	5.20	7.85	5.20	7.75
5.10	10.00	5.30	8.70	5.30	8.10	5.30	8.05
		5.40	8.85	5.40	8.25	5.40	8.30
		5.50	9.00	5.60	8.60	5.50	8.45
		5.60	9.10	5.80	8.85	5.60	8.60
		5.80	9.25	6.00	9.10	5.80	8.90
		6.00	9.40	6.20	9.25	6.00	9.10
		6.20	9.55	6.40	9.45	6.20	9.25
		6.40	9.65	6.60	9.60	6.40	9.40
		6.60	9.80	6.80	9.75	6.60	9.55
		6.90	10.00	7.00	9.90	6.80	9.70
							(ppts.)

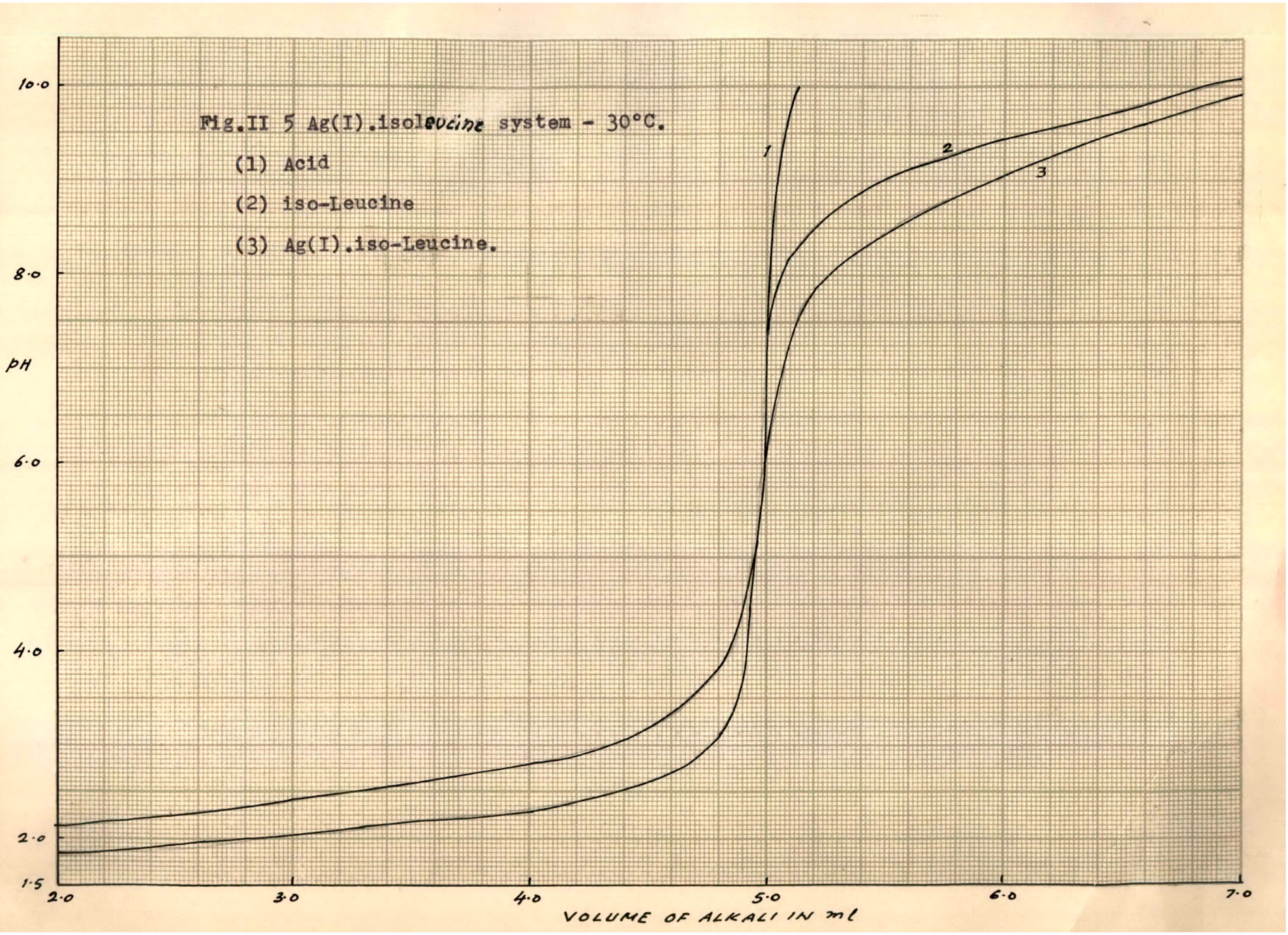


Fig.II 5 Ag(I).isoleucine system - 30°C.
(1) Acid
(2) iso-Leucine
(3) Ag(I).iso-Leucine.
1
2
3
10·0
8·0
6·0
4·0
2·0
1·5
pH
2·0
3·0
4·0
5·0
6·0
7·0
VOLUME OF ALKALI IN ml

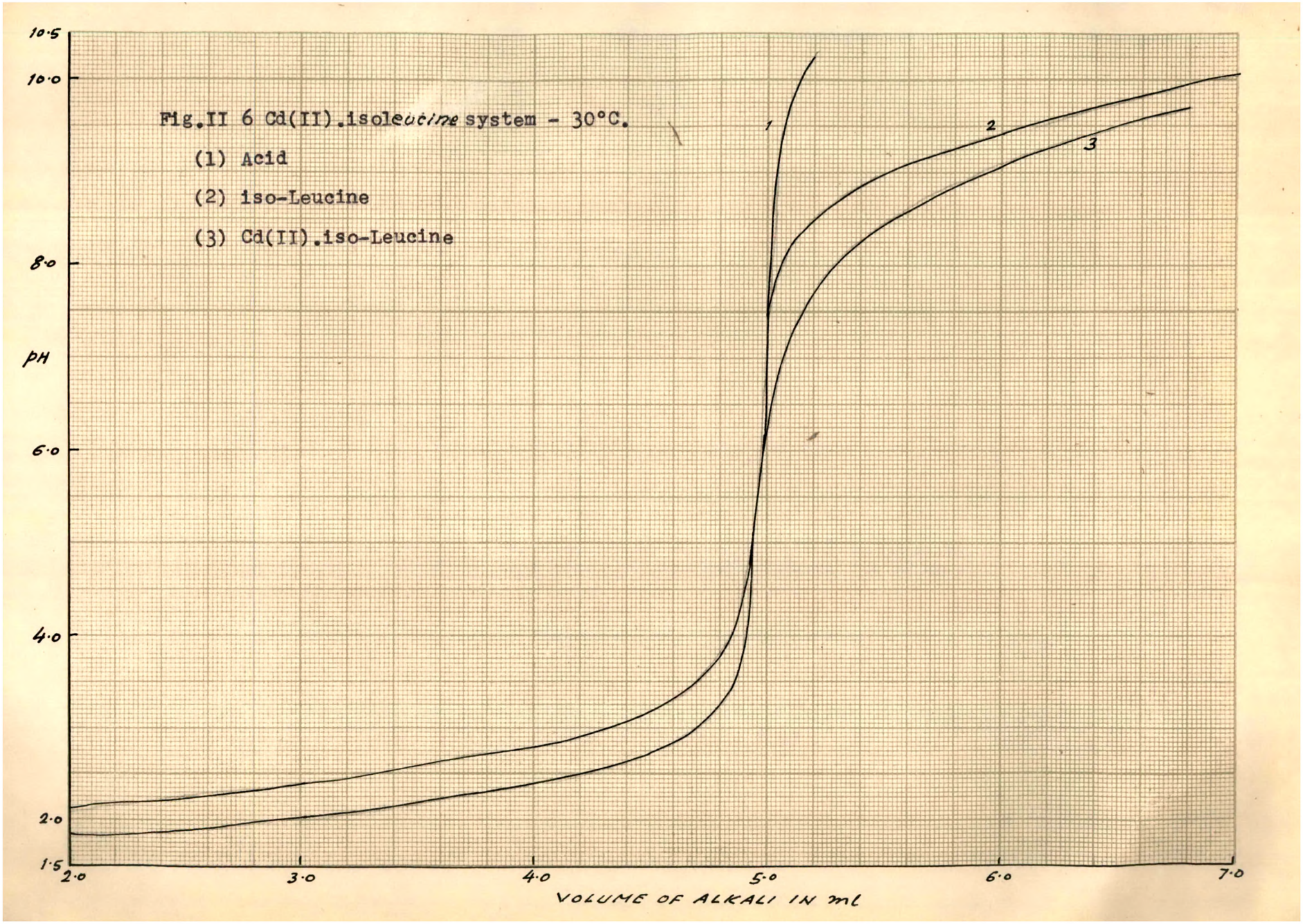


Fig.II 6 Cd(II).isoleucine system - 30°C.
(1) Acid
(2) iso-Leucine
(3) Cd(II).iso-Leucine
1
2
3
10·5
10·0
8·0
6·0
4·0
2·0
1·5
pH
2·0
3·0
4·0
5·0
6·0
7·0
VOLUME OF ALKALI IN ml

Table II 1.6

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.02M T_I° = 0.01M T_M° = 0.001M

Perchloric acid		Aspartic acid		Ni(II)		Be(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.65	1.00	1.80	1.00	1.80	1.00	1.80
2.00	1.80	2.00	1.95	2.00	1.95	2.00	1.95
2.50	1.85	3.00	2.15	3.00	2.15	3.00	2.15
3.00	2.00	4.00	2.40	4.00	2.40	4.00	2.40
3.60	2.10	4.40	2.55	4.40	2.55	4.40	2.55
3.80	2.20	4.60	2.70	4.60	2.70	4.60	2.70
4.00	2.25	4.80	2.80	4.80	2.80	4.80	2.80
4.20	2.35	5.00	2.90	5.00	2.90	5.00	2.90
4.40	2.50	5.20	3.00	5.20	3.00	5.20	3.00
4.60	2.70	5.40	3.10	5.40	3.10	5.40	3.10
4.70	2.85	5.60	3.25	5.60	3.25	5.60	3.25
4.80	3.10	5.80	3.40	5.80	3.40	5.80	3.40
4.90	3.65	6.00	3.50	6.00	3.45	6.00	3.50
4.94	5.25	6.20	3.65	6.40	3.70	6.20	3.60
4.96	5.75	6.40	3.75	6.80	3.95	6.40	3.70
5.00	8.30	6.60	3.90	7.00	4.10	6.66	3.85
5.02	9.00	6.80	4.05	7.10	4.20	6.80	4.00
5.04	9.45	7.00	4.30	7.20	4.30	7.00	4.20
5.06	9.70	7.10	4.45	7.30	4.45	7.10	4.35
5.08	9.85	7.20	4.60	7.40	4.70	7.20	4.50
5.10	10.00	7.25	4.80	7.50	4.95	7.30	4.70
		7.30	5.00	7.55	5.15	7.40	4.95
		7.35	5.25	7.60	5.30	7.50	5.25
		7.40	5.60	7.65	5.55	7.55	7.45
		7.45	6.35	7.70	5.80	7.60	5.65
		7.50	7.50	7.75	6.10	7.65	5.90
		7.55	8.00	7.80	6.35	7.70	6.15
		7.60	8.25	7.85	6.65	7.75	6.40
		7.70	8.55	7.90	7.00	7.80	6.65
		7.80	8.70	7.95	7.60	7.85	6.95
		7.90	8.85	8.00	8.00	7.90	7.45
		8.00	8.95	8.10	8.40	8.00	8.20
		8.20	9.15	8.20	8.60		(ppts.)
		8.60	9.45	8.30	8.75		
		9.00	9.65	8.40	8.90		
		9.40	9.90		(ppts.)		

Table II 1.7

N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.02M T°_{L} = 0.01M T°_{M} = 0.001M

Perchloric acid		Aspartic acid		Zn(II)		Cd(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.60	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.65	1.00	1.80	1.00	1.80	1.00	1.80
2.00	1.80	2.00	1.95	2.00	1.95	2.00	1.95
2.50	1.85	3.00	2.15	3.00	2.15	3.00	2.15
3.00	2.00	4.00	2.40	4.00	2.40	4.00	2.40
3.60	2.10	4.40	2.55	4.40	2.55	4.40	2.55
3.80	2.20	4.60	2.70	4.60	2.70	4.60	2.70
4.00	2.25	4.80	2.80	4.80	2.80	4.80	2.80
4.20	2.35	5.20	2.90	5.00	2.90	5.00	2.90
4.00	2.50	5.20	3.00	5.20	3.00	5.20	3.00
4.60	2.70	5.40	3.10	5.40	3.10	5.40	3.10
4.70	2.85	5.60	3.25	5.60	3.25	5.60	3.25
4.80	3.10	5.80	3.40	5.80	3.40	5.80	3.40
4.90	3.65	6.00	3.50	6.00	3.50	6.00	3.50
4.94	5.25	6.20	3.65	6.20	3.65	6.20	3.65
4.96	5.75	6.40	3.75	6.40	3.75	6.40	3.75
5.00	8.30	6.60	3.90	6.80	4.05	6.60	3.90
5.02	9.00	6.80	4.05	7.00	4.25	6.80	4.05
5.04	9.45	7.00	4.30	7.20	4.60	7.00	4.30
5.06	9.70	7.10	4.45	7.30	4.85	7.10	4.45
5.08	9.85	7.20	4.60	7.40	5.20	7.20	4.00
5.10	9.00	7.25	4.80	7.45	5.45	7.25	4.80
		7.30	5.00	7.50	5.65	7.35	5.25
		7.35	5.25	7.55	5.90	7.40	5.60
		7.40	5.60	7.60	6.15	7.45	6.15
		7.45	6.35	7.65	6.40	7.50	6.50
		7.50	7.50	7.70	6.70	7.55	6.70
		7.55	8.00	7.75	7.70	7.60	7.00
		7.60	8.25	7.80	7.25	7.65	7.25
		7.70	8.55	7.90	7.80	7.70	7.50
		7.80	8.70	8.00	8.20	7.75	7.70
		7.90	8.85		(ppts.)	7.80	7.85
		8.00	8.95			7.90	8.10
		8.20	9.15			8.00	8.30
		8.60	9.45				(ppts.)
		9.00	9.65				
		9.40	9.90				

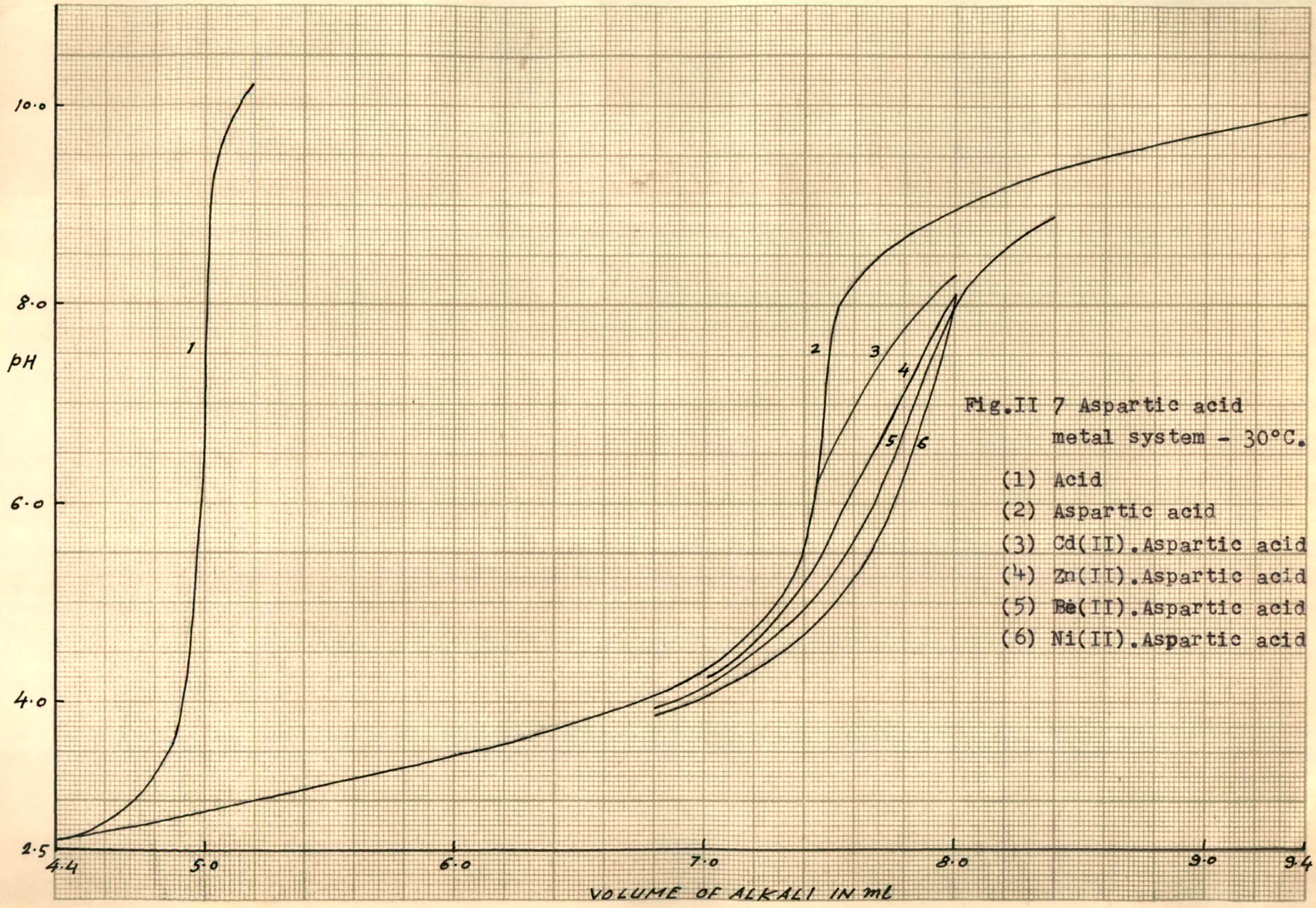


Fig.II 7 Aspartic acid metal system - 30°C.

(1) Acid
(2) Aspartic acid
(3) Cd(II).Aspartic acid
(4) Zn(II).Aspartic acid
(5) Be(II).Aspartic acid
(6) Ni(II).Aspartic acid

Table II 2.1a

$\bar{n}_H$, $\bar{n}$, pL data for Cd(II) glycin system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.20	1.00_0	5.00	5.12	0.12	0.48_0	4.44_3
7.30	1.00_0	5.00	5.14	0.14	0.56_0	4.34_8
7.40	1.00_0	5.00	5.17	0.17	0.68_0	4.25_3
7.50	1.00_0	5.00	5.20	0.20	0.80_0	4.15_9
7.80	0.99_8	5.01	5.30	0.29	1.15_9	3.87_0
7.90	0.98_8	5.03	5.33	0.30	1.19_9	3.77_9
8.00	0.98_4	5.04	5.37	0.33	1.31_9	3.68_5
8.10	0.97_2	5.05	5.41	0.36	1.43_8	3.59_2
8.20	0.96_4	5.09	5.47	0.38	1.51_7	3.49_6

Table II 2.2a

$\bar{n}_H$, $\bar{n}$, pL data for Cd(II) α-Alanine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.20	1.00_0	5.00	5.09	0.09	0.36_0	4.56_8
7.30	1.00_0	5.00	5.11	0.11	0.44_0	4.47_2
7.40	1.00_0	5.00	5.13	0.13	0.52_0	4.37_6
7.50	0.99_6	5.00	5.15	0.15	0.60_2	4.28_0
7.60	0.99_6	5.01	5.18	0.17	0.68_3	4.18_5
7.70	0.99_2	5.02	5.20	0.18	0.72_5	4.08_6
7.80	0.98_8	5.03	5.24	0.21	0.85_0	3.99_2
8.10	0.98_0	5.07	5.35	0.28	1.14_1	3.70_7
8.20	0.97_6	5.09	5.40	0.31	1.26_7	3.61_3
8.30	0.96_8	5.11	5.45	0.34	1.40_2	3.52_1
8.40	0.95_6	5.14	5.50	0.36	1.50_2	3.42_6
8.50	0.94_0	5.17	5.57	0.40	1.69_6	3.34_7

Table II 2.3a

$\bar{n}_H$, $\bar{n}$, pL data for Cd(II) β-Alanine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
8.20	0.98_0	5.04	5.14	0.10	0.40_7	3.91_1
8.25	0.98_0	5.05	5.16	0.11	0.44_8	3.86_3
8.30	0.98_0	5.05	5.17	0.12	0.48_9	3.83_4
8.35	0.97_6	5.06	5.19	0.13	0.53_2	3.76_6
8.40	0.97_6	5.06	5.20	0.14	0.57_3	3.71_9
8.45	0.79_2	5.07	5.22	0.15	0.61_6	3.67_1
8.50	0.97_2	5.08	5.24	0.16	0.65_7	3.62_3

Table II 2.4a

$\bar{n}_H$, $\bar{n}$, pL data for Cd(II) Leucine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.50	1.00_0	5.00	5.13	0.13	0.52_0	4.17_5
7.55	1.00_0	5.01	5.15	0.14	0.55_9	4.12_8
7.60	0.99_6	5.01	5.16	0.15	0.60_2	4.08_0
7.65	0.99_6	5.02	5.18	0.16	0.64_2	4.03_2
7.70	0.99_6	5.02	5.19	0.17	0.68_2	3.98_4
7.75	0.99_2	5.03	5.21	0.18	0.72_5	3.93_6
7.80	0.98_8	5.03	5.23	0.20	0.80_9	3.89_0
8.15	0.96_8	5.09	5.38	0.29	1.19_6	3.55_9
8.20	0.96_4	5.10	5.40	0.30	1.24_3	3.51_2
8.25	0.95_6	5.11	5.43	0.32	1.33_6	3.46_7
8.30	0.95_2	5.13	5.46	0.33	1.38_3	3.42_0
8.35	0.94_8	5.14	5.49	0.35	1.47_3	3.37_4
8.40	0.94_4	5.15	5.52	0.37	1.56_3	3.32_9

Table II 2.5a

$\bar{n}_H$, $\bar{n}$, pL data for Cd(II) iso-Leucine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.45	1.00_0	5.00	5.13	0.13	0.52_0	4.24_6
7.55	1.00_0	5.01	5.15	0.14	0.55_8	4.14_8
7.65	0.99_2	5.02	5.17	0.15	0.61_1	4.05_0
7.75	0.99_2	5.03	5.20	0.17	0.69_2	3.95_4
7.80	0.98_8	5.04	5.22	0.18	0.72_8	3.90_6
7.85	0.99_2	5.04	5.23	0.19	0.76_8	3.85_8
7.95	0.98_4	5.05	5.26	0.21	0.85_3	3.76_2
8.35	0.95_6	5.13	5.44	0.31	1.29_4	3.38_5
8.40	0.94_8	5.15	5.47	0.32	1.34_6	3.33_8
8.45	0.94_0	5.17	5.51	0.34	1.44_2	3.29_3
8.50	0.93_2	5.19	5.54	0.35	1.49_6	3.24_6
8.55	0.92_8	5.21	5.57	0.36	1.54_5	3.20_9

Table II 2.6a

$\bar{n}_H$, $\bar{n}$, pL data for Cd(II) Aspartic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.00	1.00_8	7.48	7.60	0.12	0.47_6	4.68_3
7.10	1.00_8	7.48	7.62	0.14	0.55_6	4.58_6
7.20	1.00_4	7.49	7.64	0.15	0.59_8	4.48_9
7.30	1.00_4	7.49	7.66	0.17	0.67_7	4.39_2
7.40	1.00_4	7.49	7.68	0.19	0.75_7	4.29_6
7.50	1.00_0	7.50	7.70	0.20	0.80_0	4.20_0
7.60	1.00_0	7.50	7.73	0.23	0.92_0	4.10_4
7.70	1.00_0	7.50	7.75	0.25	1.00_0	4.00_7
7.80	0.99_6	7.51	7.78	0.27	1.08_4	3.91_3
7.90	0.99_2	7.52	7.81	0.29	1.16_9	3.81_7
8.00	0.98_0	7.55	7.85	0.30	1.22_3	3.72_0
8.10	0.98_0	7.56	7.89	0.33	1.34_6	3.62_6
8.20	0.98_0	7.58	7.93	0.35	1.42_7	3.53_1
8.30	0.97_2	7.61	7.99	0.38	1.56_1	3.43_8

Table II 2.1b

$\bar{n}_H$, $\bar{n}$, pL data for Ag(I) glycine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.75	0.99_6	5.01	5.13	0.12	0.48_2	3.89_4
7.80	0.99_6	5.02	5.15	0.13	0.52_2	3.84_6
7.85	0.99_2	5.03	5.17	0.14	0.56_4	3.79_8
7.90	0.98_8	5.03	5.19	0.16	0.64_7	3.75_2
7.95	0.98_4	5.03	5.20	0.17	0.69_1	3.70_4
8.00	0.98_4	5.04	5.22	0.18	0.73_1	3.65_6
8.05	0.97_6	5.05	5.25	0.20	0.81_6	3.61_0
8.10	0.97_2	5.06	5.27	0.21	0.86_3	3.56_3
8.35	0.94_4	5.14	5.42	0.28	1.18_3	3.32_9
8.40	0.93_6	5.16	5.45	0.29	1.23_5	3.28_2
8.45	0.92_8	5.18	5.49	0.31	1.33_2	3.23_7
8.50	0.92_4	5.20	5.53	0.33	1.42_3	3.19_2
8.55	0.91_6	5.22	5.57	0.35	1.52_2	3.14_8

Table II 2.2b

$\bar{n}_H$, $\bar{n}$, pL data for Ag(I) α-Alanine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.65	0.99_2	5.02	5.15	0.13	0.52_4	4.12_6
7.70	0.99_2	5.02	5.17	0.15	0.60_4	4.08_0
7.75	0.99_2	5.03	5.19	0.16	0.64_5	4.03_2
7.80	0.98_8	5.03	5.20	0.17	0.68_7	3.98_4
7.85	0.98_8	5.04	5.22	0.18	0.72_8	3.93_6
7.90	0.98_8	5.04	5.24	0.20	0.80_9	3.89_0
8.20	0.97_6	5.09	5.38	0.29	1.18_7	3.60_9
8.25	0.96_8	5.10	5.41	0.31	1.27_9	3.56_4
8.30	0.96_8	5.11	5.43	0.32	1.32_0	3.51_6
8.35	0.95_6	5.12	5.45	0.33	1.37_8	3.46_9
8.40	0.95_6	5.14	5.48	0.34	1.41_9	3.42_2
8.45	0.94_4	5.16	5.51	0.35	1.47_9	3.37_5
8.50	0.94_0	5.18	5.54	0.36	1.52_7	3.32_8

Table II 2.3b

$\bar{n}_H$, $\bar{n}$, pL data for Ag(I) β-Alanine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.80	0.99_6	5.01	5.11	0.10	0.40_2	4.31_0
7.85	0.99_6	5.02	5.13	0.11	0.44_2	4.26_2
7.90	0.99_2	5.02	5.14	0.12	0.48_4	4.21_4
7.95	0.99_2	5.02	5.15	0.13	0.52_4	4.16_6
8.00	0.98_8	5.02	5.16	0.14	0.56_7	4.11_8
8.05	0.98_8	5.03	5.18	0.15	0.60_7	4.07_0

Table II 2.4b

$\bar{n}_H$, $\bar{n}$, pL data for Ag(I) Leucine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.65	0.99_6	5.01	5.14	0.13	0.52_2	4.02_6
7.70	0.99_6	5.02	5.16	0.14	0.56_2	3.97_8
7.75	0.99_2	5.03	5.18	0.15	0.60_4	3.93_0
7.80	0.98_8	5.04	5.20	0.16	0.64_7	3.88_2
7.85	0.98_8	5.04	5.21	0.17	0.68_8	3.83_4
7.90	0.98_4	5.05	5.23	0.18	0.73_1	3.78_6
8.25	0.95_6	5.12	5.40	0.28	1.16_9	3.45_9
8.30	0.95_2	5.13	5.43	0.30	1.25_7	3.41_3
8.35	0.94_8	5.14	5.45	0.31	1.30_5	3.36_6
8.40	0.94_4	5.16	5.48	0.32	1.35_2	3.32_8
8.50	0.93_6	5.19	5.55	0.36	1.54_6	3.22_9

Table II 2.5b

$\bar{n}_H$, $\bar{n}$, pL data for Ag(I) iso-Leucine system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.75	0.99_2	5.03	5.16	0.13	0.52_4	3.94_6
7.80	0.99_2	5.04	5.18	0.14	0.56_4	3.89_8
7.85	0.98_8	5.04	5.20	0.16	0.64_7	3.85_2
7.90	0.98_8	5.05	5.22	0.17	0.68_7	3.80_4
7.95	0.98_4	5.05	5.24	0.19	0.77_2	3.75_8
8.00	0.98_4	5.06	5.26	0.20	0.81_2	3.71_0
8.25	0.96_8	5.10	5.38	0.28	1.15_4	3.47_7
8.30	0.96_4	5.12	5.41	0.29	1.20_0	3.43_0
8.35	0.95_6	5.13	5.44	0.31	1.29_4	3.38_6
8.40	0.94_8	5.15	5.48	0.33	1.38_8	3.34_0
8.45	0.94_0	5.17	5.51	0.34	1.44_2	3.39_3
8.50	0.93_2	5.19	5.54	0.35	1.49_7	3.24_6

Table II 2.6c

$\bar{n}_H$, $\bar{n}$, pL data for Zn(II) Aspartic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.90	1.01_9	7.42	7.55	0.13	0.51_1	5.78_6
6.00	1.01_9	7.42	7.57	0.15	0.59_0	5.68_9
6.10	1.01_9	7.43	7.59	0.16	0.62_3	5.59_1
6.20	1.01_6	7.44	7.61	0.17	0.67_0	5.49_3
6.40	1.01_2	7.45	7.65	0.20	0.79_1	5.29_8
6.60	1.00_8	7.46	7.69	0.23	0.91_3	5.10_4
6.80	1.00_8	7.47	7.72	0.25	0.99_3	4.90_8
7.00	1.00_8	7.48	7.75	0.27	1.07_2	4.71_2
7.10	1.00_8	7.48	7.77	0.29	1.15_1	4.61_6
7.20	1.00_4	7.49	7.79	0.30	1.19_5	4.51_8
7.30	1.00_4	7.49	7.89	0.32	1.27_5	4.42_2
7.40	1.00_4	7.49	7.83	0.34	1.36_0	4.32_4
7.50	1.00_0	7.50	7.85	0.35	1.40_0	4.22_9
7.60	1.00_0	7.50	7.87	0.37	1.48_0	4.13_3
7.70	1.00_0	7.50	7.88	0.38	1.52_0	4.03_5

Table II 2.6d

$\bar{n}_H$, $\bar{n}$, pL data for Ni(II) Aspartic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.00	1.05_1	7.31	7.51	0.20	0.76_4	6.71_2
5.10	1.04_3	7.33	7.54	0.21	0.80_8	6.61_1
5.20	1.03_5	7.35	7.57	0.22	0.85_2	6.51_1
5.30	1.03_1	7.37	7.59	0.22	0.85_5	6.40_9
5.40	1.02_7	7.38	7.61	0.23	0.89_6	6.31_0
5.50	1.02_7	7.39	7.64	0.25	0.97_6	6.21_2
5.60	1.02_3	7.40	7.66	0.26	1.01_8	6.10_7
5.70	1.01_9	7.41	7.68	0.27	1.06_2	6.01_4
5.80	1.01_9	7.42	7.70	0.28	1.10_1	5.91_3
5.90	1.01_9	7.42	7.72	0.30	1.17_9	5.81_9
6.00	1.01_9	7.42	7.74	0.32	1.25_8	5.72_3
6.10	1.01_9	7.43	7.75	0.32	1.25_8	5.62_3
6.20	1.01_6	7.44	7.77	0.33	1.30_1	5.52_4
6.30	1.01_6	7.45	7.79	0.34	1.34_0	5.42_6
6.40	1.01_2	7.45	7.80	0.35	1.38_5	5.32_8

Table II 2.6e

$\bar{n}_H$, $\bar{n}$, pL data for Be(II) Aspartic acid system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.10	1.04_3	7.33	7.45	0.12	0.46_2	6.59_4
5.20	1.03_5	7.35	7.48	0.13	0.51_5	6.49_4
5.40	1.02_7	7.38	7.54	0.16	0.62_5	6.29_5
5.60	1.02_3	7.40	7.60	0.20	0.78_4	6.10_1
5.70	1.01_9	7.41	7.62	0.21	0.82_6	6.00_2
5.80	1.01_9	7.42	7.64	0.22	0.86_5	5.90_4
6.00	1.01_9	7.42	7.67	0.25	0.98_3	5.70_9
6.20	1.01_6	7.44	7.71	0.27	1.06_4	5.51_1
6.40	1.01_2	7.45	7.75	0.30	1.18_0	5.31_7
6.50	1.00_8	7.46	7.77	0.31	1.23_1	5.22_0
6.60	1.00_8	7.46	7.79	0.33	1.31_0	5.12_4
6.70	1.00_8	7.47	7.81	0.34	1.35_0	5.02_4
6.80	1.00_8	7.47	7.83	0.36	1.42_9	4.92_9
6.90	1.00_8	7.47	7.84	0.37	1.46_9	4.83_2
7.00	1.00_8	7.48	7.86	0.38	1.50_8	4.73_4

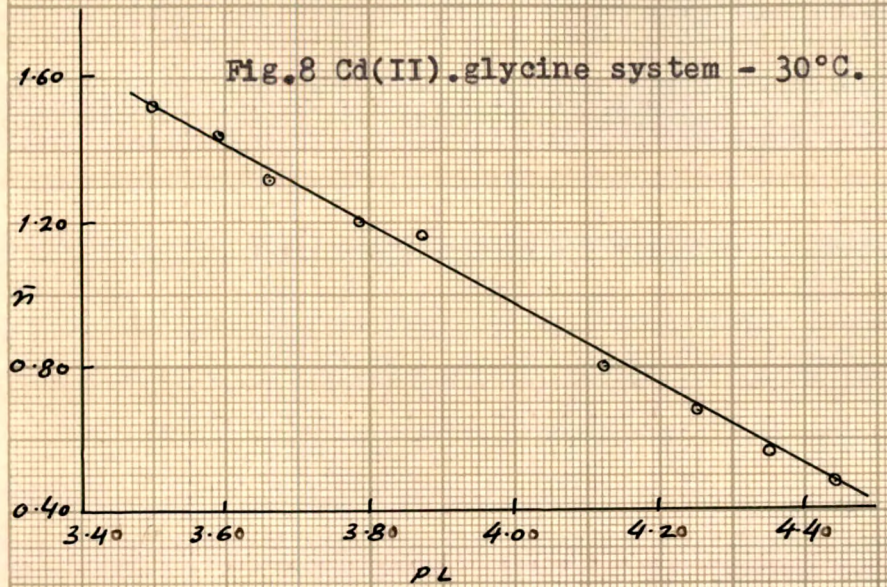


Fig.8 Cd(II).glycine system - 30°C.

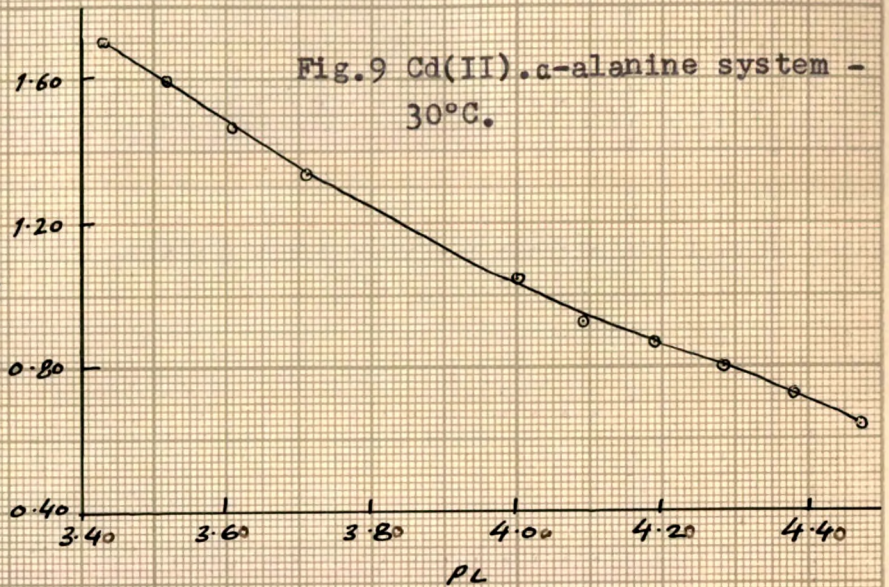


Fig.9 Cd(II).α-alanine system - 30°C.

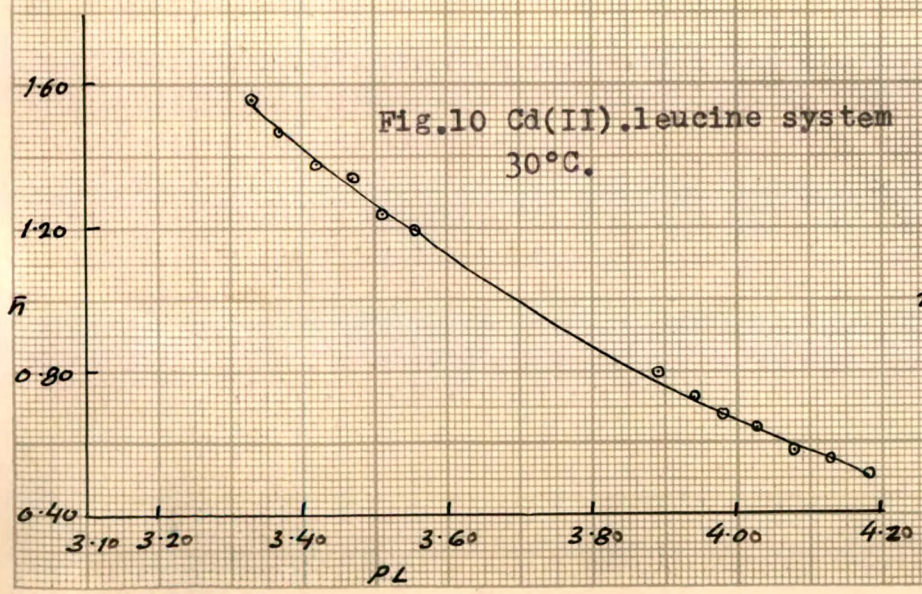


Fig.10 Cd(II).leucine system 30°C.

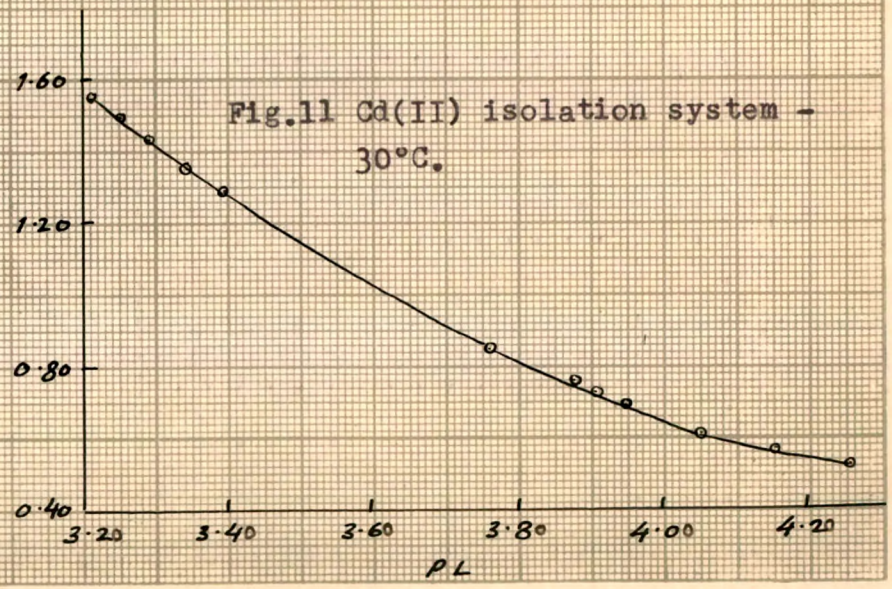


Fig.11 Cd(II) isolation system - 30°C.

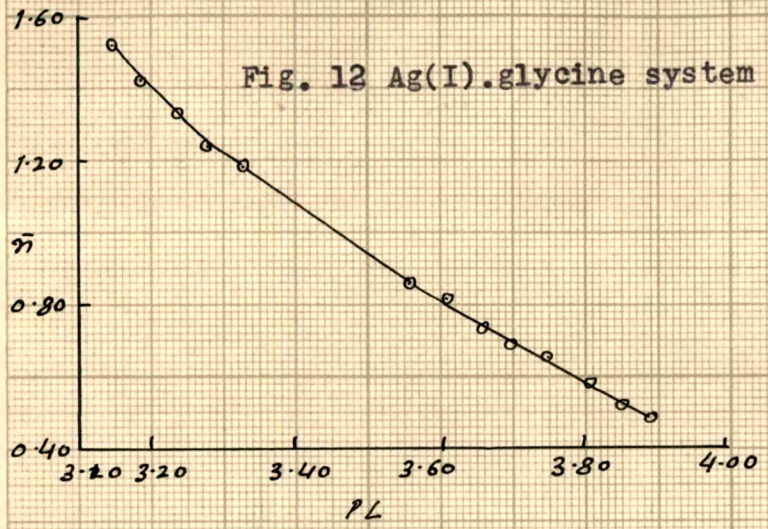


Fig. 12 Ag(I).glycine system - 30°C.

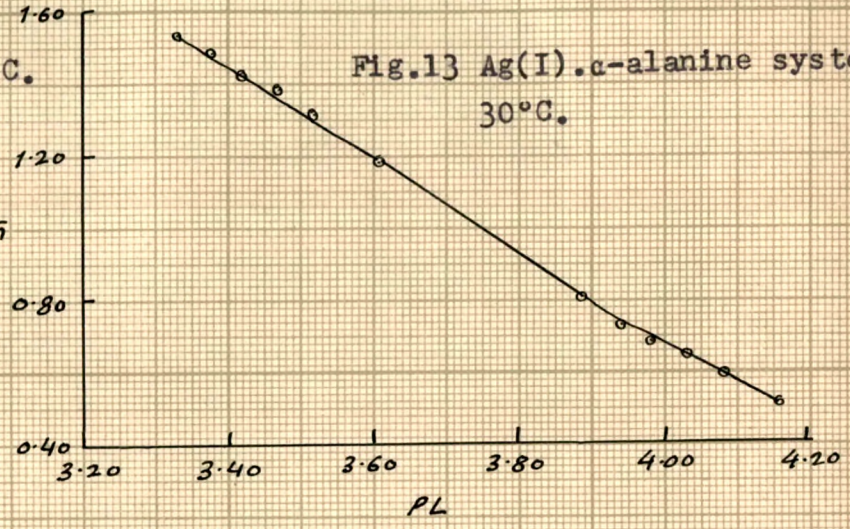


Fig.13 Ag(I).α-alanine system - 30°C.

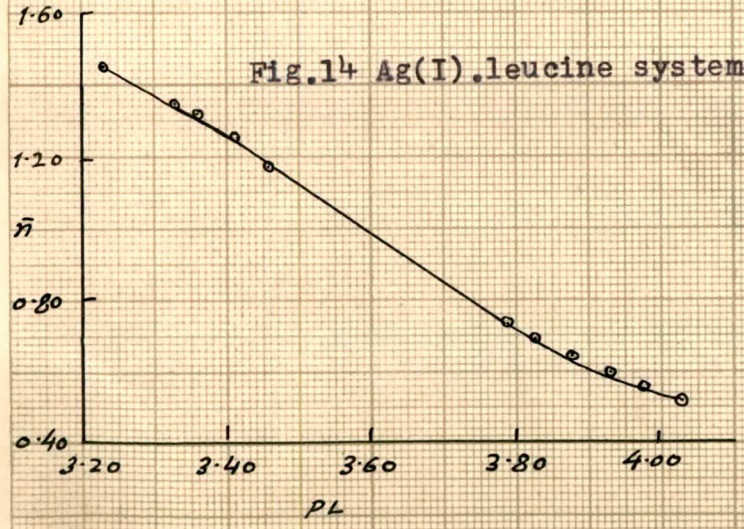


Fig.14 Ag(I).leucine system-30°C.

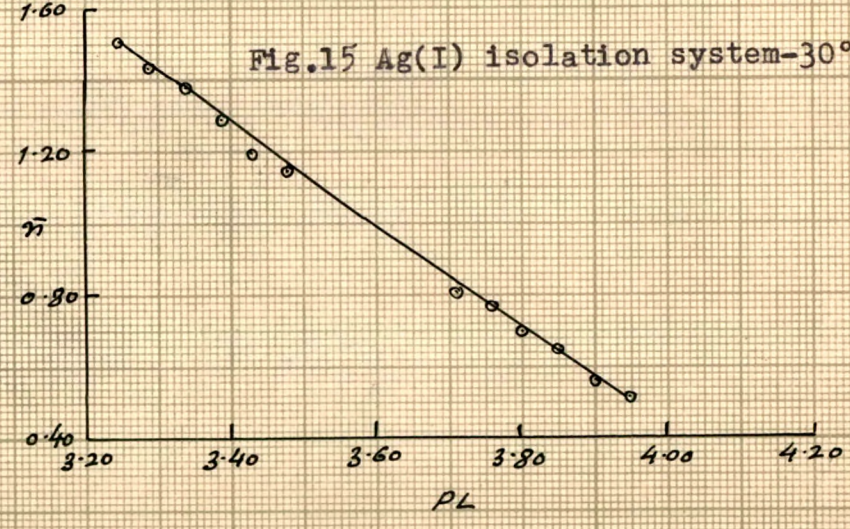


Fig.15 Ag(I) isolation system-30°C.

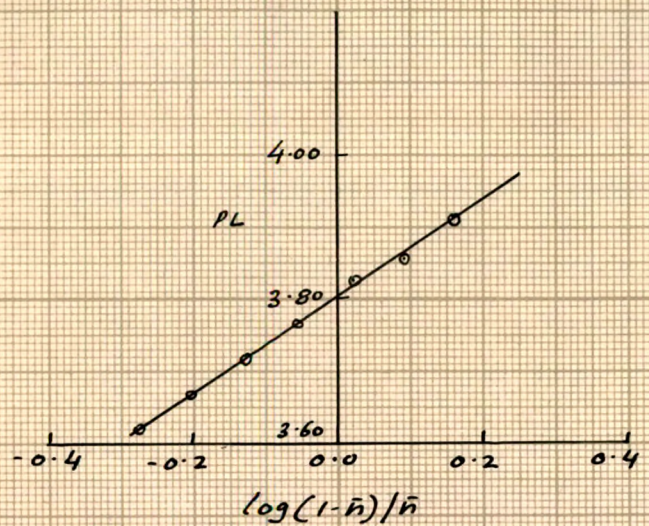


Fig.16 Cd(II).β-alanine system - 30°C.

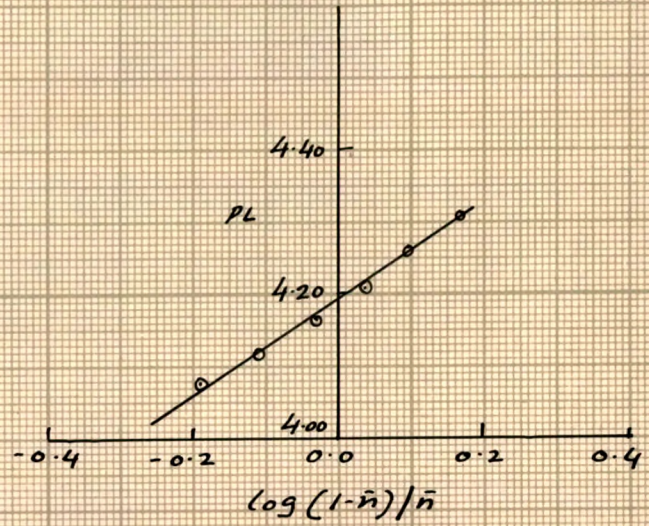


Fig.17 Ag(I).β-alanine system - 30°C.

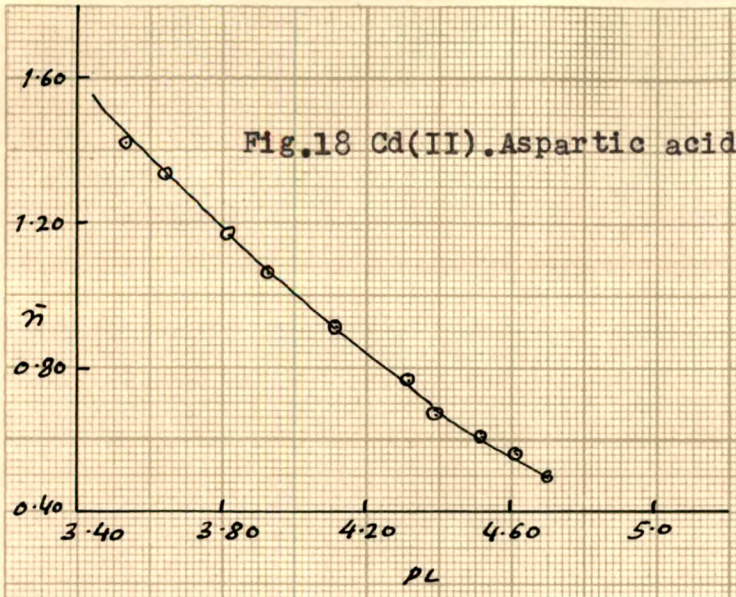


Fig.18 Cd(II).Aspartic acid system -30°C.

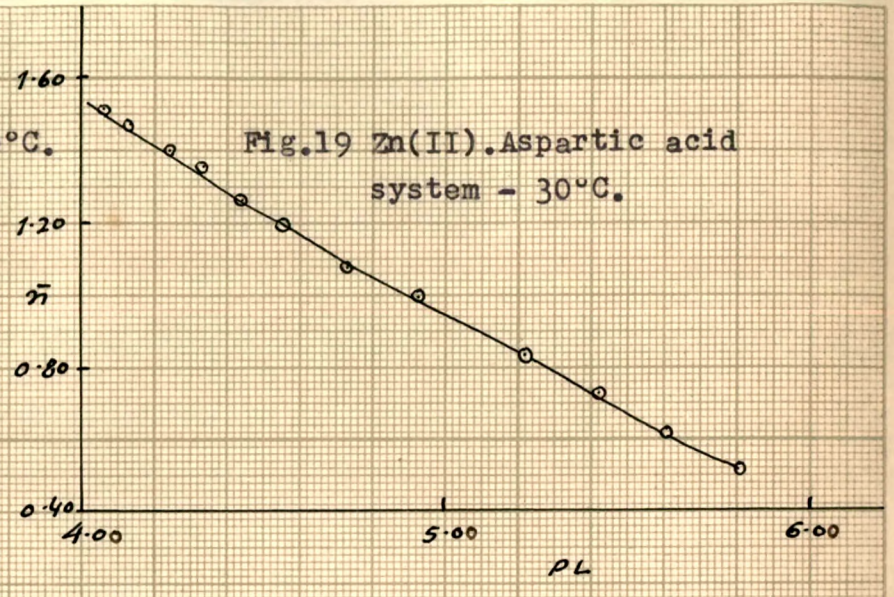


Fig.19 Zn(II).Aspartic acid system - 30°C.

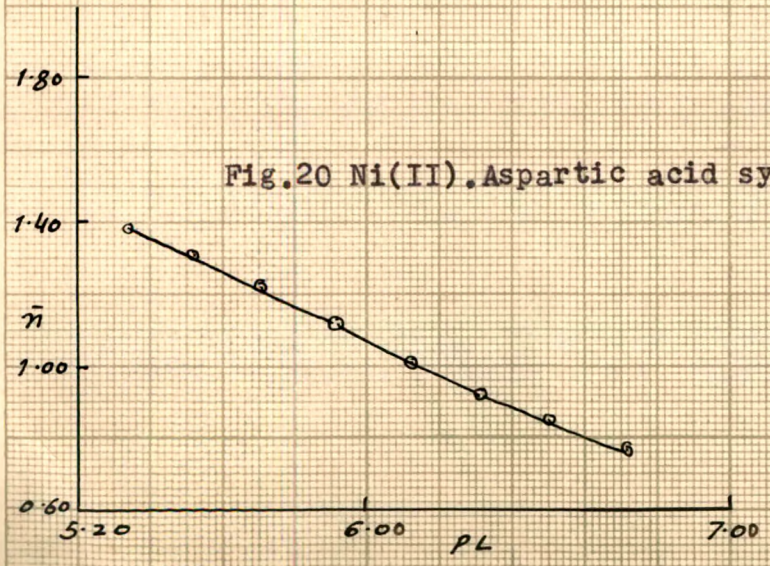


Fig.20 Ni(II).Aspartic acid system-30°C.

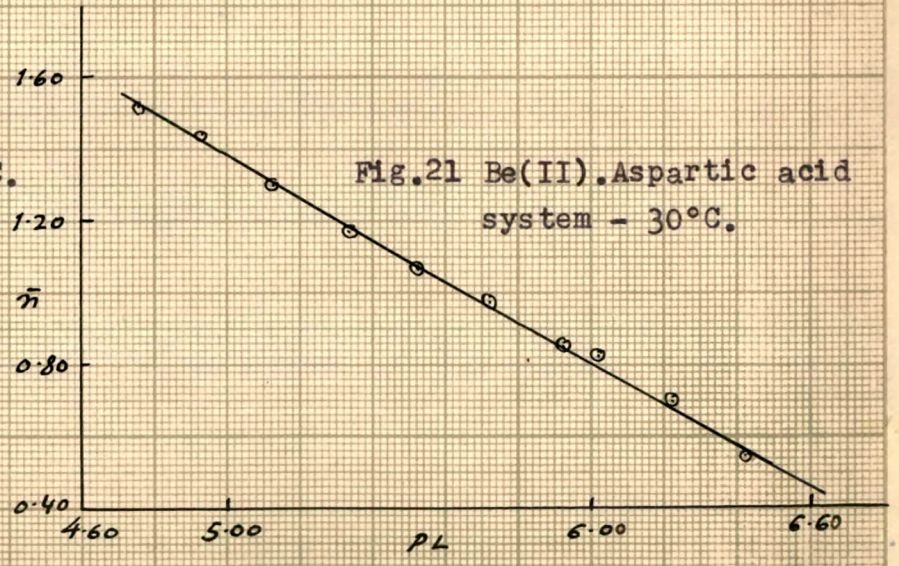


Fig.21 Be(II).Aspartic acid system - 30°C.

Table II 3.1a

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Cd(II) glycine system - 30°C.

$\bar{n}$	pL	y x 10^4	x x 10^{-4}	log β_2	log K_1	log K_2
0.48	4.44	-2.5422	-1.0613	7.86	4.21	3.65
0.56	4.35	-2.8491	-1.4619	7.87	4.20	3.67
0.68	4.25	-3.7791	-2.3194	7.94	4.24	3.70
0.80	4.16	-5.7820	-4.1508	7.98	4.34	3.64
1.20	3.78	3.6144	6.6400	7.91	4.34	3.57
1.32	3.69	2.0200	4.3392	7.94	4.24	3.70
1.44	3.60	1.3028	3.1971	7.98	4.17	3.81
1.52	3.50	0.9244	2.9187	7.96	4.21	3.75

log β_2 = 7.93 ± 0.04
log K_1 = 4.24 ± 0.05
log K_2 = 3.69 ± 0.06

Table II 3.2a

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Cd(II) α-Alanine system - 30°C.

$\bar{n}$	pL	y x 10^4	x x 10^{-4}	log β_2	log K_1	log K_2
0.44	4.47	-2.3191	-0.9438	7.71	4.26	3.45
0.52	4.38	-2.5985	-1.2854	7.77	4.29	3.48
0.60	4.28	-2.8582	-1.8368	7.74	4.28	3.46
0.68	4.18	-3.2162	-2.7252	7.70	4.26	3.44
1.14	3.71	4.1758	11.9785	7.70	4.31	3.39
1.27	3.61	1.1959	6.6375	7.75	4.19	3.56

log β_2 = 7.73 ± 0.03
log K_1 = 4.27 ± 0.03
log K_2 = 3.46 ± 0.04

Table II 3.3a

$\bar{n}$, pL, $\log(1-\bar{n})/\bar{n}$ and pL - $\log(1-\bar{n})/\bar{n}$ data of Cd(II) β-Alanine system - 30°C.

$\bar{n}$	pL	$\log (1-\bar{n})/\bar{n}$	pL-$\log (1-\bar{n})/\bar{n}$
0.40_7	3.91_1	0.16_4	3.74_7
0.44_8	3.86_3	0.09_1	3.77_2
0.48_9	3.83_4	0.01_9	3.81_5
0.53_2	3.76_6	$\bar{1}.94_4$	3.82_2
0.57_3	3.71_9	$\bar{1}.87_3$	3.84_7
0.61_6	3.67_1	$\bar{1}.79_5$	3.87_6
0.65_7	3.62_3	$\bar{1}.71_8$	3.90_5

$\log K_1 = 3.83 \pm 0.05$

Table II 3.4a

$\bar{n}$, pL, y, x, $\log \beta_2$, $\log K_1$ and $\log K_2$ data of Cd(II) Leucine system - 30°C.

$\bar{n}$	pL	y x 10^4	x x 10^{-4}	$\log \beta_2$	$\log K_1$	$\log K_2$
0.52	4.18	-1.6396	-2.0371	7.59	4.01	3.58
0.60	4.08	-1.8033	-2.9113	7.52	3.98	3.54
0.68	3.99	-1.9277	-4.5469	7.38	3.77	3.61
1.34	3.47	1.1632	6.5767	7.48	3.89	3.59
1.38	3.42	0.9551	6.2032	7.46	3.94	3.52

$\log \beta_2 = 7.48 \pm 0.04$

$\log K_1 = 3.92 \pm 0.06$

$\log K_2 = 3.56 \pm 0.04$

Table II 3.5a

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Cd(II) iso-Leucine system - 30°C.

$\bar{n}$	pL	y x 10^4	x x 10^{-4}	log β_2	log K_1	log K_2
0.68	3.95	-1.8939	-4.6282	7.37	4.00	3.37
0.72	3.91	-2.0905	-5.6228	7.36	4.00	3.36
0.77	3.86	-2.4259	-7.3800	7.34	3.99	3.35
0.85	3.76	-3.2604	-13.3246	7.26	3.82	3.44
1.29	3.39	1.0918	9.9742	7.28	3.93	3.35
1.35	3.34	0.8438	8.4890	7.29	3.91	3.38

log β_2 = 7.31 ± 0.03
log K_1 = 3.94 ± 0.05
log K_2 = 3.37 ± 0.02

Table II 3.6a

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Cd(II) Aspartic acid system - 30°C.

$\bar{n}$	pL	y x 10^5	x x 10^{-5}	log β_2	log K_1	log K_2
0.68	4.39	-0.5216	-16.8052	8.03	4.54	3.49
0.76	4.30	-0.6318	-25.8953	8.05	4.56	3.49
1.17	3.82	0.4546	73.9188	8.03	4.51	3.48
1.22	3.72	0.2911	67.5409	7.97	4.62	3.35
1.35	3.63	0.1646	43.5314	8.06	4.47	3.59
1.43	3.53	0.1127	39.1179	8.06	4.48	3.58

log β_2 = 8.03 ± 0.03
log K_1 = 4.53 ± 0.05
log K_2 = 3.50 ± 0.07

Table II 3.1b

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Ag(I) glycine system - 30°C.

$\bar{n}$	pL	y x 10^3	x x 10^{-3}	log B_2	log K_1	log K_2
0.48	3.89	-7.1667	-0.3764	6.99	3.59	3.40
0.52	3.85	-7.6673	-0.4356	6.98	3.56	3.42
0.56	3.80	-8.0298	-0.5187	6.94	3.52	3.42
0.65	3.75	-10.4451	-0.6858	7.00	3.62	3.38
0.69	3.70	-11.1596	-0.8430	6.96	3.53	3.43
0.73	3.66	-12.3569	-1.0292	6.94	3.46	3.48
1.33	3.24	7.0043	1.1682	6.95	3.57	3.38
1.42	3.19	5.2385	0.8916	6.99	3.47	3.52

$\log \beta_2 = 6.97 \pm 0.02$
$\log K_1 = 3.54 \pm 0.05$
$\log K_2 = 3.43 \pm 0.04$

Table II 3.2b

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Ag(I) α-Alanine system - 30°C.

$\bar{n}$	pL	y x 10^4	x x 10^{-4}	log β_2	log K_1	log K_2
0.52	4.12	-1.4281	-2.3390	7.48	3.83	3.65
0.60	4.08	-1.8033	-2.9113	7.57	3.94	3.63
0.65	4.03	-1.9899	-3.5998	7.54	3.92	3.62
0.69	3.98	-2.1258	-4.4244	7.50	3.84	3.66
0.73	3.94	-2.3551	-5.3998	7.48	3.78	3.70
1.28	3.56	1.6599	7.0817	7.53	3.86	3.73
1.32	3.52	1.3658	6.4175	7.51	3.85	3.66
1.38	3.47	1.0719	5.5278	7.51	3.86	3.65
1.42	3.42	0.8892	5.2503	7.49	3.91	3.58
1.48	3.38	0.7096	4.5164	7.50	3.80	3.70
1.53	3.33	0.6172	4.1475	7.51	3.86	3.65

$\log \beta_2 = 7.51 \pm 0.02$
$\log K_1 = 3.85 \pm 0.03$
$\log K_2 = 3.66 \pm 0.03$

Table II 3.3b

$\bar{n}$, pL, $\log(1-\bar{n})/\bar{n}$ and pL - $\log(1-\bar{n})/\bar{n}$ data of Ag(I) β-Alanine system - 30°C.

$\bar{n}$	pL	$\log (1-\bar{n})/\bar{n}$	pL-$\log (1-\bar{n})/\bar{n}$
0.40_2	4.31_0	0.17_3	4.13_7
0.44_2	4.26_2	0.10_1	4.16_1
0.48_4	4.21_4	0.03_8	4.17_6
0.52_4	4.16_6	$\bar{1}.96_8$	4.19_8
0.56_7	4.11_8	$\bar{1}.88_3$	4.23_5
0.60_7	4.07_0	$\bar{1}.81_1$	4.25_9

$\log K_1 = 4.20 \pm 0.04$

Table II 3.4b

$\bar{n}$, pL, y, x, $\log \beta_2$, $\log K_1$ and $\log K_2$ data of Ag(I) Leucine system - 30°C.

$\bar{n}\bar{n}$	pL	y x 10^4	x x 10^{-4}	$\log \beta_2$	$\log K_1$	$\log K_2$
0.60	3.93	-1.2766	-4.1125	7.25	3.81	3.44
0.64	3.88	-1.3488	-4.9791	7.20	3.76	3.44
0.69	3.83	-1.5049	-6.2499	7.18	3.73	3.45
0.73	3.79	-1.6668	-7.6294	7.16	3.69	3.47
1.17	3.46	1.9851	16.9271	7.18	3.79	3.39
1.26	3.41	1.2457	11.0715	7.21	3.66	3.55
1.30	3.37	1.0157	9.9540	7.20	3.71	3.49
1.35	3.32	0.8059	8.8882	7.18	3.75	3.43

$\log \beta_2 = 7.20 \pm 0.02$
$\log K_1 = 3.74 \pm 0.04$
$\log K_2 = 3.46 \pm 0.04$

Table II 3.5b

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Ag(I) iso-Leucine system - 30°C.

$\bar{n}$	pL	y x 10^3	x x 10^{-3}	log β_2	log K_1	log K_2
0.52	3.95	-9.6553	-0.3459	7.19	3.67	3.52
0.56	3.90	-10.1090	-0.4120	7.15	3.62	3.53
0.65	3.85	-13.1432	-0.5450	7.21	3.72	3.49
0.69	3.80	-14.0429	-0.6697	7.15	3.64	3.51
0.89	3.71	-21.8623	-1.2213	7.16	3.62	3.54
1.15	3.47	22.6288	1.9198	7.15	3.71	3.44
1.29	3.39	10.9186	0.9974	7.18	3.55	3.63
1.50	3.23	5.0951	0.5888	7.20	3.54	3.66

log β_2 = 7.17 ± 0.02
log K_1 = 3.63 ± 0.05
log K_2 = 3.54 ± 0.06

Table II 3.6c

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Zn(II) Aspartic acid system - 30°C.

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log β_2	log K_1	log K_2
0.79	5.30	-0.7506	-28.8786	9.82	5.74	4.08
1.20	4.52	0.1987	120.8000	9.79	5.74	4.05
1.28	4.42	0.1202	97.7657	9.84	5.74	4.10
1.40	4.23	0.0594	88.3200	9.84	5.77	4.07
1.48	4.13	0.0416	80.3075	9.87	5.71	4.16

log β_2 = 9.83 ± 0.02
log K_1 = 5.74 ± 0.02
log K_2 = 4.09 ± 0.03

Table II 3.6d

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Ni(II) Aspartic acid system - 30°C.

$\bar{n}$	pL	y x 10^7	x x 10^{-7}	log β_2	log K_1	log K_2
0.76	6.71	-1.6239	-10.0750	12.49	7.13	5.36
0.81	6.61	-1.7367	-15.3761	12.49	7.12	5.32
0.85	6.51	-1.8888	-23.0000	12.40	7.11	5.29
1.18	5.82	0.4330	68.9711	12.40	7.14	5.26
1.26	5.72	0.2544	54.2192	12.46	7.08	5.38

$\log \beta_2 = 12.44 \pm 0.03$
$\log K_1 = 7.12 \pm 0.02$
$\log K_2 = 5.32 \pm 0.04$

Table II 3.6e

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data of Be(II) Aspartic acid system - 30°C.

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log β_2	log K_1	log K_2
0.83	6.00	-4.8824	-6.8823	11.29	6.52	4.77
1.18	5.32	1.3697	21.8028	11.35	6.57	4.78
1.23	5.22	0.8874	20.1740	11.34	6.58	4.76
1.31	5.12	0.5570	16.8849	11.38	6.53	4.85
1.43	4.93	0.2830	15.5755	11.39	6.52	4.87

$\log \beta_2 = 11.35 \pm 0.03$
$\log K_1 = 6.54 \pm 0.03$
$\log K_2 = 4.81 \pm 0.04$

Table II 4.0

Proton ligand stability constants of various amino acids-30°C.

Ligand (L)	$P_{K_2}H$	$P_{K_1}H$
Glycine	2.23 ± (0.01)	9.58 ± (0.01)
α-Alanine	2.22 ± (0.03)	9.71 ± (0.01)
β-Alanine	3.41 ± (0.01)	10.05 ± (0.01)
Leucine	2.22 ± (0.01)	9.61 ± (0.02)
iso-Leucine	2.24 ± (0.01)	9.63 ± (0.01)
Aspartic acid	3.60 ± (0.01)	9.60 ± (0.01)

Table II 5.1

Formation constants of various amino acids chelates-30°C.

Ligand (L)		Cd(II)	Ag(I)	Cu(II)	Ni(II)	Be(II)	Zn(II)
Glycine	$\log K_1$	4.24±0.05	3.54±0.05	8.11±0.03*	5.90±0.06*	6.58±0.03*	5.22±0.03*
	$\log K_2$	3.69±0.06	3.43±0.04	6.67±0.09*	5.05±0.07*	5.59±0.10*	4.37±0.04*
α-Alanine	$\log K_1$	4.27±0.03	3.85±0.02	8.21±0.06*	5.55±0.03*	6.74±0.05*	5.17±0.03*
	$\log K_2$	3.46±0.03	3.66±0.03	6.84±0.08*	4.53±0.05*	5.69±0.08*	4.10±0.07*
β-Alanine	$\log K_1$	3.83±0.05	4.20±0.04	-	-	-	-
Leucine	$\log K_1$	3.92±0.06	3.74±0.04	-	-	-	-
	$\log K_2$	3.56±0.04	3.46±0.04	-	-	-	-
iso-Leucine	$\log K_1$	3.94±0.05	3.63±0.02	-	-	-	-
	$\log K_2$	3.37±0.02	3.54±0.06	-	-	-	-
Aspartic acid	$\log K_1$	4.53±0.05	-	-	7.12±0.02	6.54±0.03	5.74±0.02
	$\log K_2$	3.50±0.07	-	-	5.32±0.04	4.81±0.04	4.09±0.03

* Values are taken from literature for comparison.

Table II 5.2

Formation constants of various oxy acids chelates - 30°C.

Ligand(L)		Cu(II)**	Ni(II)*	Be(II)*
Glycollic acid	$\log K_1$	6.19 ± 0.03	4.76 ± 0.03	7.51 ± 0.02
	$\log K_2$	-	4.35 ± 0.03	5.94 ± 0.04
Lactic acid	$\log K_1$	6.50 ± 0.04	5.01 ±00.06	7.94 ± 0.04
	$\log K_2$	-	4.59 ± 0.03	6.47 ± 0.07
Malic acid	$\log K_1$	8.43 ± 0.01	5.50 ± 0.02	9.09 ± 0.08
	$\log K_2$	-	4.89 ± 0.03	-

* Values are taken from literature for comparison.

** Metal ion and ligand are in 1:1 ratio.

References :

1. Bjerrum,J., "Metal Amine Formation in Aqueous Solution", p.Hase and Sons, Copenhagen (1941).
2. Bjerrum,J., Chem.Revs., 46, 381 (1950).
3. Irving,H.M., and Rossotti,H.S., J.Chem.Soc., 3397 (1953).
4. Ley,Z., Elecktrochem, 10, 954 (1904).
5. Dubsky,I.J.V., and Langer,A., Collection Czechoslov.Chem. Commun; 8, 435 (1936).
6. Li,N.C., and Doddy,E., J.Amer.Chem.Soc., 72, 1891 (1950).
7. Maley,L.E., and Mellor,D.P., Australian J.Sci., Research, 2A, 579 (1949).
8. Volshtein,L.M., and Sektora, Izvest., Platiny i.Drug. Blagorod.Metal., 27, 20 (1952).
9. Kopanica,M., and Dolczal,J., Chem.Listy., 51, 1052 (1957).
10. Ramel,M.M., and Paris,M.R., Bull.Soc.Chim., (FV), 4, 1359 (1969).
11. Perrin,D.D., J.Chem.Soc., 290 (1959).
12. Baumann,E., Rother,A., and Trapmann,H., Arch.Pharm., 292, 29 (1959).
13. Sagnini,D., Curran,C., and Quagliano,J.V., Spectrochim. Acta., 16, 540 (1960).
14. Porcelli,G., and Gaudiano,A., Rend.1st Super.Samita, 24, 291 (1961).
15. Nakamoto,K., Morimoto,Y., and Martell,A.E., J.Amer.Chem. Soc., 83, 4528 (1961).
16. Fedorov,I.A., and Balankneva,T.A., Zh.Neorg.Khim., 7, 312 (1962).

17. Smith,J.H., and Crucikshank,A.M., Donoghue,J.T., and Pysz,J.F., J.Inor.Chem., 1, 148 (1962).

18. Batyaev,I.M., and Larionov,S.N., Izv.Sibirsk.Otd.Akad. Nauk. S.S.S.R., No.12, 69 (1962).

19. Li,N.C., Seruggs,R.L., and Becker,E.D., J.Amer.Chem.Soc., 84, 4650 (1962).

20. Mathur,H.B., J.Ind.Chem.Soc., 2(7), 257 (1964).

21. Gupta,S.S., Garg,D.P., and Marwah,S.D., J.Prakt.Chem., 24 (5-6), 274 (1964).

22. Andren,R.G., and Buzo,T.J., 'Anales Real.Soc.Espan. Fis.Quim.Ser'., B. 59(6), 427 (1963).

23. Sharma,V.S., Mathur,H.B., Biswas,A.B., Indian J.Chem., 2(7), 257 (1964).

24. Rao,G.N., and Subramanya,R.S., Proc.Indian Acad.Sci., Sect., A60(3), 169 (1964).

25. Fedorov,I.A., Balakaeva,T.A., and Kuchunova,A.N., Zh. Neorg.Khim., 11(7), 1969 (1966).

26. Azizov,Yu.M., Mijtakova,A.Kh., and Toropova,Zh.Neorg.Khim., 12(3), 661 (1967).

27. Gergely,A., and Naypal,I., Acta.Phy.Chim.Derbrecina., 11, 113 (1965).

28. Kustin,K., Pasternack,R.F., and Weinstock,E.M., J.Amer. Chem.Soc., 88(20), 4610 (1966).

29. Gergely,A., and Mojzes,J., Magy.Key. Folyoirat, 72(7), 292 (1966).

30. Sekhon,B.S., Singh,P.P., Chopra,S.L., Indian J.Chem., 9(5), 485 (1971).

31. Tanner,S.P., and Choppin,G.R., Inorg.Chem.,7(10),2046 (1968).

32. Sahu,K.N., and Bhattacharya,A.K, J.Ind.Chem.Soc., 46(4), 325 (1969).

33. Rastogi,R.K., and Srivastava,A.K., Indian J.Chem., 7(7), 717 (1969).

34. Chapurina,L.F., and Ablav,A.V., Zh.Neorg.Khim., 14(6), 1521 (1969).

35. Theophile,T., Inorg,Chem.Acta., 4(3), 395 (1970).

36. Yoshinovi,K., and Yukimasa,K., Chem.Pharm.Bull., 9(18), 1921 (1970).

37. Herlinger,A.W., Wenhold,S.L., and Long,I.V., II, J.Amer. Chem.Soc., 92(22), 6474,6481 (1970).

38. Dutta,S.P., Lebermann,R., and Rabin,B.R., Nature, 183, 745 (1959).

39. Bretton,P., J.Chem.Phys., 55, 53, 61 (1958).

40. Bretton.P., J.Chem.Phys., 54, 827 (1957).

41. Sunderson,R., and Sundaram,A.K., Indian J.Chem., 9(2), 148 (1971).

42. Kodama, Mutsuo; Takahashi, Shozo., Bull.Chem.Soc.,Japan, 44(3), 697 (1971).

43. Huenze, Rudolf; Guethert, Axel; Matthes, Harbert.; Z.Phys.Chem., 241(3-4) (1969).

44. Dreyer,Rolf; Redlich, Juergen; Syhre, Rosemarie; Z. Phys.Chem., 238(5-6), 417 (1968).

45. Tasi-Teh Lai, and Song., Jey Wey, Rev.Polarogr., 14(3-6), 211 (1967).

46. Herschel, Frye, Cecilia, Luschak, and Donald., Chim.Z. Naturforch., 22(3), 268 (1967).

47. Irving,H.M., and Rossotti,H.S., J.Chem.Soc., 2904 (1954).

48. Vogel,A.I., "A text book of quantitative inorganic analysis", The ELBS and Longmans Green and Co.,Ltd., p.204. (1962).

49. Chidambaram,M.V., "Formation and stability of some amino acid chelates", Ph.D. thesis, M.S.University, Baroda (1971).

50. Hearon,J., and Gilbert,J.B., J.Amer.Chem.Soc., 77, 2594(1955).

51. Rossotti,F.I.C., and Rossotti,H.S., Acta.Chem.Scand., 9, 1166 (1955).

52. Chidambaram,M.V., and Bhattacharya,P.K., J.Ind.Chem.Soc., 47, 881 (1970).

53. Chidambaram,M.V., and Bhattacharya,P.K., Indian J.Chem., 8, 941 (1970).

54. Schwarzenbach,G., Ackermann,H., Maissen,B., abd Anderegg,G., Helv.Chim.Acta., 35, 2337 (1952).

55. Irving,H.M., and William,R.J.P., Nature, 162, 746 (1948).

56. Lewis,J., and Wilkins,R.G., "Modern Coordination Chemistry", Interscience Publishers Inc., New York, p.255 (1960).

57. Reddy,M.V., and Bhattacharya,P.K., J.Prakt.Chemic.Band., 312 (1970).

58. Reddy,M.V., and Bhattacharya,P.K., Indian J.Chem., 7(3), 282 (1969).

59. Reddy,M.V., "Study of the chelates of some oxy and thio-compounds with transition and nontransition metal ions", Ph.D. thesis, M.S.University (1970).

60. Panchal,B.R., "Study of the metallic complexes containing VIth group ligand atoms", Ph.D. thesis, M.S.University, Baroda (1972).