CHAPTER II

Binary Metal β-dicarbonyl systems

Section A Metal-β-diketone systems
Section B Metal-β-ketoester systems
Section C Metal-β-ketoimine systems

Section A

According to Bjerrum the complex formation is a stepwise reaction as follows :

$$M + L \rightleftharpoons ML \qquad (1.1)$$

$$ML + L \rightleftharpoons ML_2 \qquad (1.2)$$

$$ML_{i-1} + L \rightleftharpoons ML_i \qquad (1.3)$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad (1.4)$$

where M = metal ion; L = ligand.

The charges on the ligand ions have not been shown. The equilibrium constant governing each step is, termed the stepwise formation constant.

For a complex of the type $[ML_2]$,

$$k_1 = \frac{[ML_1]}{[M][L]} \qquad (1.5)$$

$$k_2 = \frac{[ML_2]}{[ML][L]} \qquad (1.6)$$

and

$$\beta_2 = k_1.k_2 = \frac{[ML_2]}{[M][L]^2} \qquad (1.7)$$

In solution there is competition between the hydrogen ion and metal ion to combine with the ligand ion. If it is L^{2-}, two hydrogen ions can combine in steps -

$$L^{2-} + H^+ \rightleftharpoons LH^- \qquad (1.8)$$

$$LH^- + H^+ \rightleftharpoons LH_2 \qquad (1.9)$$

Equilibrium constants govern each step and are known as first and second proton ligand stability constants,

K_1^H and K_2^H.

The function $\bar{n}_H$, can be defined as average number of protons bound per not complex bound ligand. If the total concentration of the ligand is T_L°, and that of metal ion is M, the concentration of the free ligand is equal to $T_L^\circ - \bar{n}\ T_M^\circ$, where $\bar{n}$ is the average number of ligands bound per metal ion. For a complex ML_2 the expression for $\bar{n}$ is as follows -

$$\bar{n} = \frac{k_1[L] + 2k_1.k_2\,[L]^2}{1 + k_1[L] + k_1.k_2\,[L]^2} \qquad (2.0)$$

It is presumed that the polynuclear complexes and proton bearing complexes do not exist in solution. The free ligand exists in solution, in the form of undissociated molecule H_2L and the ions H_L^- and L^{2-}.

$$T_L^\circ - \bar{n}\ T_m = H_2L + HL^- + L^{2-} \qquad (2.1)$$

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

$$-\log L = pL = \log\left[\frac{1 + {}^PK_1^H\left(\frac{1}{\text{antilog }B}\right) + {}^PK_1^H.\,{}^PK_2^H\left(\frac{1}{\text{antilog }B}\right)^2}{T_L^\circ - \bar{n}.T_M^\circ} \cdot \frac{V^\circ + V''}{V^\circ}\right] \qquad (2.2)$$

Bjerrum[1] 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 logk_2, respectively. The values are, however, not very precise. The plots of $\bar{n}$ against pL give the formation curves. Various computations of $\bar{n}$ and pL values have been attempted to get the precise values of the formation constants. Amongst them the method of least square[2,3] is supposed to be most precise and has been used in the present study of metal β-diketone chelates.

The study of acetylacetone complexes of transition and non transition metals in solution have been reported earlier[4]. Stability constants of β-diketone complexes of lanthanide elements have also been reported[5,6]. Stability constants of Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) complexes with mono-thio β-diketones have been worked out[7]. Calvin and Wilson[8] have compared the stability constants of the complexes of β-diketones and 3-alkyl substituted derivatives of diketones. Stability constants of benzoylacetone and dibenzoylmethane chelates of Cu(II) and Ni(II) have been determined by Van Uitert, Fernelius and Doughlas[9], specially with a view to study steric effects. Fernelius and Byrant[10] have also reported stability constants of some metal acetylacetonates.

In the present investigation the main interest is to study the mixed ligand formation constants K^{MA}_{MAL}; where M = Cu(II) or Ni(II), A = dipyridyl or o-phenanthroline or polycarboxylic amino acids, and L = β-diketones. Such systems have been reported in the later chapter. However, for comparing the values of formation constants of the ternary complexes with the corresponding values of binary systems, K^{M}_{ML} are required under identical conditions. It is observed that the β-diketone complexes of Ni(II) and Cu(II) have not been studied by using Irving-Rossotti titration technique. The formation constants of the complexes of the ligands acetylacetone, benzoylacetone and dibenzoylmethane with Cu(II) and Ni(II) have been worked out in the present chapter.

Experimental :

Irving-Rossotti titration technique[11] 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. The ligands used in the present study are sparingly soluble in water and hence all titrations were carried out in 50% dioxan medium. Dioxan was purified by the known method[12]. Double distilled water was prepared as usual.

The other details are as follows :

(a) Ligands and other chemicals :

The ligands used were all A.R. pure. Purity was checked by noting the M.P. or B.P.. Ligands used were acetylacetone (BDH), benzoylacetone (Fluka), dibenzoylmethane (K.Light). The standard solutions were prepared by dissolving the weighed quantity in known volume of purified dioxan. Since dioxan solvent is easily oxidised, fresh solutions of ligands were prepared prior to titration.

(i) Sodium hydroxide : The solution was prepared by dissolving 50 g of sodium hydroxide (Chemapol), in 500 ml of double distilled water and was allowed to stand for two days. The solution was filtered through G_4 sintered glass crucible. This was standardised against standard oxalic acid solution and stored out of contact with carbon dioxide using a soda lime guard tube. The solution was diluted to get solutions of required concentration.

(ii) Sodium perchlorate : The required quantity of sodium perchlorate (A.R.,Riedel) was weighed and dissolved in 500 ml of double distilled water to prepare 1M solution.

(iii) Perchloric acid solution : The perchloric acid (Riedel, analysed) supplied was of 80% concentration. A definite volume of the acid was dissolved in 500 ml of double distilled water to get a solution of approximate 0.2M strength. The exact concentration was determined by titrating against standard sodium hydroxide solution.

(iv) Metal salt solution : In order to avoid the complexing tendencies of the anion, the perchlorates of Ni(II) 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 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). The amounts of metal present were estimated. From this stock solution, required concentrations of metal perchlorates were prepared by proper dilution.

Apparata :

All glassware used were of Pyrex glass. The micro-burette was calibrated to 0.01 by the method described by Vogel.[13] The measuring vessels such as micro-pipettes, measuring flasks of various capacities, pipettes etc. were calibrated by using a standard burette.

pH Meter and Accessories :

A Metrohm pH Meter of type E 350A operating on

220-240 volts and 40-60 cycles and designed for entire pH range from 0 to 14 and having glass and calomel electrode combination was used. The pH meter has readability of ± 0.05 unit and a reproducibility of 0.02 pH unit. It was calibrated with buffer of 4 and 7 pH. The calibration was intermittently checked.

Details of Irving-Rossotti titration technique :

All glassware used were of Pyrex glass and were calibrated. The titration was carried out in a 100 ml beaker having a cover provided with three holes. Through one was admitted the electrode, the other two were used for burette tip and glass stirrer. In all, three sets were prepared as follows :

1. Acid titration -
   $0.02M\ HClO_4$, $0.178M\ NaClO_4$.
2. Reagent titration -
   $0.02M\ HClO_4$, 0.02M ligand and $0.178M\ NaClO_4$.
3. Metal titration -
   $0.02M\ HClO_4$, 0.002M ligand, 0.002M metal salt solution and $0.176M\ NaClO_4$.

In all cases the total volume was 50 ml. It was so adjusted that each solution was 50% dioxan by volume. Initially ionic strength of the solution was raised to 0.2M in all the cases by the addition of required amount of neutral salt i.e. sodium perchlorate.

The titration beakers containing above solutions were allowed to stand for some time. The ratio of metal salt to ligand was maintained 1:1 in all the metal titrations in order to compare K_{MAL} with K_{ML}, under identical conditions. After addition of each poriton of alkali, pH was noted. The highest reading which remains steady was recorded in all cases. pH corrections for the dioxan solvent have been made for each reading as suggested by Van Uitert and Haas[14].

In all the equations the term B is used instead of pH, the relationship being.

$$B = -\log[H] - \left[\log\gamma + \log U_H^{\circ}\right] \qquad (2.3)$$

where γ = activity coefficient of the hydrogen ions in solution; U_H° = correction at zero ionic strength.

In case of aqueous solutions γ and U_H° are both equal to one and hence B (the pH meter reading) is equal to pH.

In the present work, studies have been carried out in 50% dioxan solution. γ and U_H° are no longer equal to unity but correspond to some value. In other words $B \neq$ pH as B the pH meter reading does not correspond to complete dissociation of hydrogen ions.

The variation of the emf of the cell with solvent composition is attributable to two effects -

(1) The partial molar free energy of the H^+ ion (at infinite dilution) varies with solvent composition. This is termed the primary medium effect.

(2) The junction error at the solution saturated KCl interface which varies with solvent composition.

The primary medium effect can be taken care of by putting the proper values of γ and U_H° in the equation.

By using the values of γ and U_H° (known in the literature for 50% dioxan solutions), the value of B was calculated for 0.02M HCl solution in 50% dioxan. It is found to be 0.1 less than the pH meter reading. This is due to the junction error in the glass electrode used. This correction was applied to all pH meter readings obtained in 50% v/v aqueous dioxan medium. 0.1 was substracted from the pH values recorded. The titration data are given in tables II A 1.1 to II A 1.3 and Figs. II A 1 to II A 3.

Determination of proton ligand and metal ligand stability constants -

It is seen in the Irving-Rossotti titration curves (fig. IIA1 to IIA3) that in the lower pH range the acid and the ligand curves 1 and 2 overlap each other. In the higher pH range, however, the ligand curve exhibits lower values of pH than the acid titration curve showing presence of more number of titratable H^+ ions due to the dissociation of the H^+ of enolic -OH. The β-dicarbonyls are weak acids due to the dissociation of the enolic -OH or in other words one of the protons on the middle carbon atom, as shown in fig.1, chapter I.

It is due to the liberation of enolic proton that the ligand has extra titratable H^+ ions.

Calculation of $\bar{n}_H$, and proton ligand stability constants :

The $\bar{n}_H$ values can be calculated by using curves 1 and 2. The horizontal distance between these two curves is used for the calculations of $\bar{n}_H$ at different pH by using the following equation :

$$\bar{n}_H = \frac{(V' + V'')\ (N + E^\circ)}{(V^\circ + V').T_L^\circ} + Y \qquad (2.4)$$

where,

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

V° = initial volume of solutions.

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

N = concentration of alkali.

E° = initial concentration of mineral acid.

T_L° = 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 values were obtained in the range $\bar{n}_H$ 0 to 1 and have been represented in table II A 3.1. The details of intermediate stages of calculations and graphs have not been given to economise space.

Calculation of metal ligand formation constants :

It is observed that the metal and ligand curves are separated from the acid curve at higher pH. This is due to the liberation of extra hydrogen ions on the coordination of the ligand with metal ion. The $\bar{n}$ values have been calculated by measuring horizontal difference in the volume of alkali required to produce the same pH in the metal and ligand titration curves and substituting it in the following equation :

$$\bar{n} = \frac{\left[(V''' - V'')\left\{N + E^\circ + T_L^\circ\,(Y - \bar{n}_H)\right\}\right]}{(V^\circ + V'').\ \bar{n}_H . T_M^\circ} \qquad (2.5)$$

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 + acid + ligand curves.

Calculation of pL :

For the calculation of pL, the equation (2.2) was used. The pL values have been recorded in tables II A 2.1a to II A 2.5b.

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.

Since metal salt and ligand have been taken in 1:1 ratio, the values of $\bar{n}$ upto $\sim$0.6 could be calculated.

The value of pL at $\bar{n}$ = 0.5 corresponds to K_{ML}^{M}. This is, however, not very accurate. Precise values have been calculated by using the method of linear plot.[15]

In this method the formation function in the region of formation of ML, reduces to the following form :

$$\bar{n} + (\bar{n} - 1)\ k_1\ (L) = 0$$

This means that log of $(1-\bar{n})/\bar{n}$ has a linear relationship with pL. The plots of log of $(1-\bar{n})/\bar{n}$ against pL in the range $\bar{n} > 0 < 1$ have been shown in fig. II A 4 to II A 8. The values of log k_1 and k_2 can be calculated, respectively, at each point on the straight lines corresponding to the two regions of $\bar{n}$, by using the following relationship -

$$\log k_n = pL - \log(1-\bar{n})/\bar{n}$$

The average of all these values was obtained and the deviation of each individual value from the average value was calculated. The average value of log k_1 with mean deviation have been presented in tables IIA2.1a to IIA2.5b. The method described above has the following advantages :

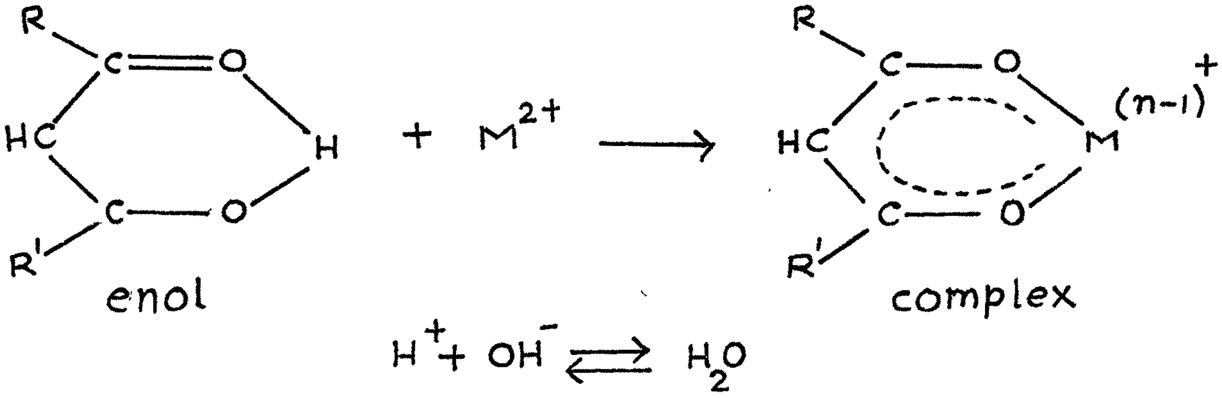
1. The value of log k_1 is not obtained only from one point ($\bar{n}$ = 0.5) and the possibility of experimental error is eliminated.

2. The points on the straight line are considered and thus the validity of $\bar{n}$ and pL data can be verified. The most divergent points, away from the linear relationship, can be discarded.

The β-diketones are characterised by one K_H value, corresponding to the enolic proton.

The order of basicity in case of β-diketone is DBM > BA > AcAc. This can be explained in terms of enol content of the diketones.[16] When the methyl group in acetylacetone is substituted by a phenyl group, the resonance energy increases for the keto as well as the enol tautomer; but much so for the enol. The enol content is 100% in dibenzoylmethane. In the enol form there is hydrogen bonding between the oxygen atoms, resulting in ring formation (fig.1). Stronger the hydrogen bonding, less is the -OH dissociation and less is the acidity of the β-diketone. In case of dibenzoylmethane and benzoylacetone as a result of strong hydrogen bonding the enolic proton is less available in the titration and this explains the higher K^{H}_{H} value.

The metal ligand formation constants are in the order DBM > BA > AcAc. The increase in stability of BA and DBM complexes is due to their high basicity. In cases of β-diketone complexes it has been shown that besides L ⟶ M σ bonding there is M ⟶ L π interaction due to the formation of six membered planar ring with delocalised π electrons.



The extent of π interaction is more in cases of benzoylacetone and dibenzoylmethane due to increase in number of phenyl groups.[16] The delocalisation of π electron clouds over the phenyl rings enhances the resonance effect in the chelate ring resulting in more stable complexes.

Table IIA 1.1

N = 0.2M V° = 50 ml. T°_L = 0.002M T°_M = 0.002M

E° = 0.02M μ = 0.2M   t = 30°C.

Perchloric acid		AcAc		Cu(II)		Ni(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	2.95	4.70	2.95	4.70	2.95	4.70	2.95
4.80	3.15	4.80	3.15	4.80	3.15	4.80	3.15
4.85	3.30	4.85	3.30	4.90	3.25	4.85	3.30
4.90	3.55	4.90	3.55	5.00	3.30	4.90	3.55
4.92	3.65	4.93	3.80	5.10	3.45	4.93	3.80
4.94	3.85	4.96	4.15	5.20	3.75	4.96	4.15
4.96	4.15	4.98	4.50	5.30	4.35	4.98	4.40
4.98	4.50	5.00	6.90	5.40	5.05	5.00	4.65
5.00	7.20	5.05	7.65	5.50	5.70	5.05	5.10
5.01	8.50	5.10	8.00	5.60	6.20	5.10	5.40
5.05	9.55	5.20	8.45	5.70	6.50	5.20	5.90
5.08	10.20	5.30	8.70	5.80	6.75	5.40	6.75
5.10	10.45	5.40	8.90	5.90	7.10	5.60	7.90
		5.60	9.15	6.00	7.60	5.80	8.65
		5.80	9.30			6.00	9.40

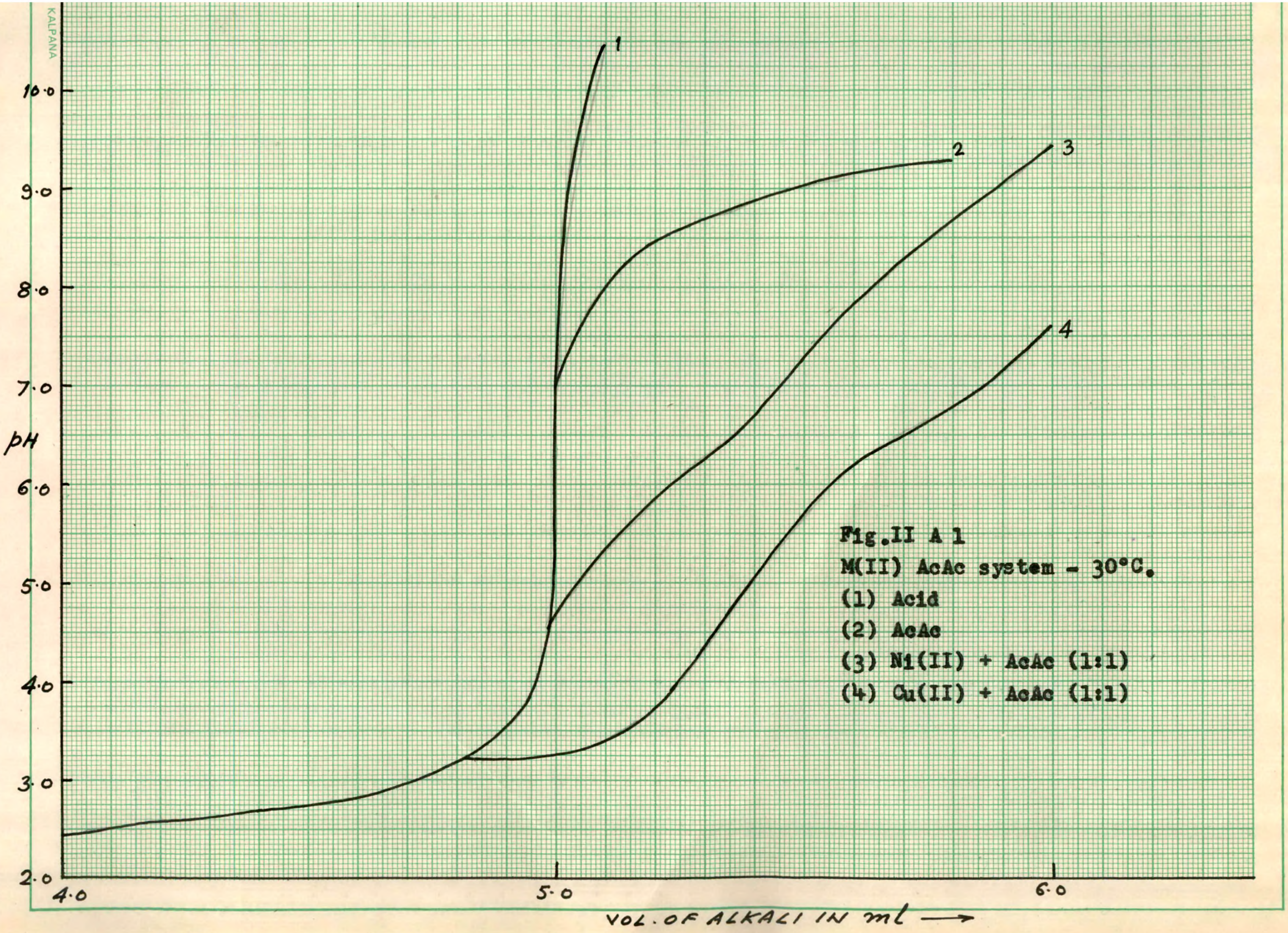


Fig.II A 1

M(II) AcAc system - 30°C.

(1) Acid

(2) AcAc

(3) Ni(II) + AcAc (1:1)

(4) Cu(II) + AcAc (1:1)

Table IIA 1.2

N = 0.2M V° = 50 ml. T°_L = 0.002M T°_M = 0.002M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		BA		Cu(II)		Ni(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	2.95	4.70	2.95	4.70	2.95	4.70	2.95
4.80	3.15	4.80	3.15	4.80	3.15	4.80	3.15
4.85	3.30	4.85	3.30	4.90	3.20	4.85	3.30
4.90	3.55	4.90	3.55	5.00	3.25	4.90	3.55
4.92	3.65	4.94	3.85	5.10	3.35	4.95	4.00
4.94	3.85	4.98	4.50	5.20	3.55	5.00	4.45
4.96	4.15	5.00	7.00	5.30	4.20	5.05	4.80
4.98	4.50	5.03	7.55	5.40	5.25	5.10	5.20
5.00	7.20	5.05	7.75	5.50	5.90	5.20	5.75
5.01	8.50	5.10	8.15	5.60	6.30	5.40	6.95
5.05	9.55	5.20	8.60	5.70	6.65	5.60	8.15
5.08	10.20	5.30	8.90	5.80	6.85	5.80	9.15
5.10	10.45	5.40	9.05	6.00	7.35	6.00	10.00
		5.60	9.35				
		5.80	9.50				

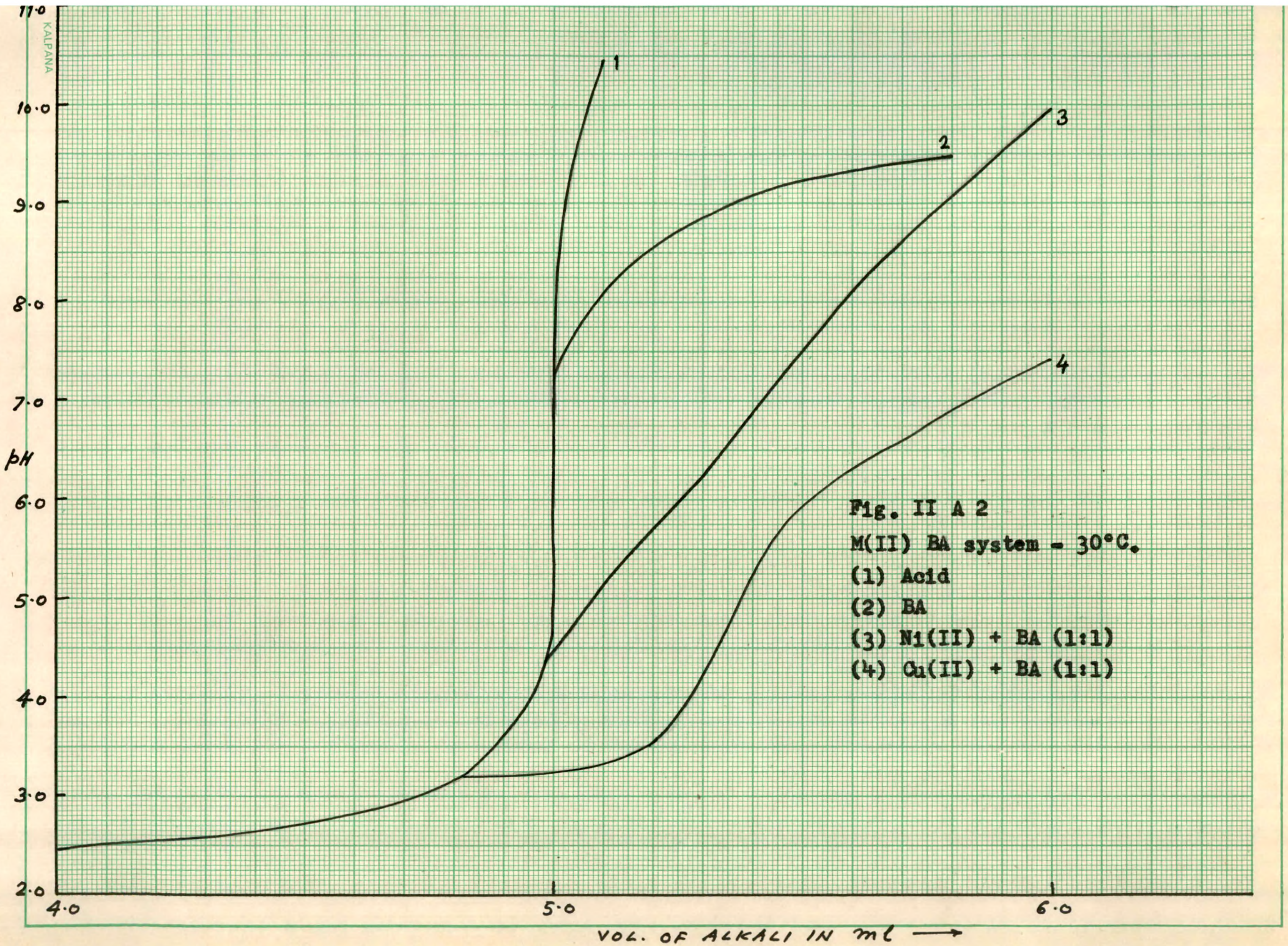


Fig. II A 2

M(II) BA system - 30°C.

(1) Acid

(2) BA

(3) Ni(II) + BA (1:1)

(4) Cu(II) + BA (1:1)

Table IIA 1.3

N = 0.2M V° = 50 ml. T_L^o = 0.002M T_M^o = 0.002M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		DBM		Ni(II)	
Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B	Vol.of alkali (in ml.)	B
0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85
4.70	2.95	4.70	2.95	4.70	2.95
4.80	3.15	4.80	3.15	4.80	3.15
4.85	3.30	4.85	3.30	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.93	3.80	4.94	3.85
4.94	3.85	4.96	4.10	4.98	4.35
4.96	4.15	4.98	4.60	5.00	4.50
4.98	4.50	5.00	7.25	5.05	4.75
5.00	7.20	5.03	7.65	5.10	5.05
5.01	8.50	5.05	7.90	5.20	5.60
5.05	9.55	5.10	8.30	5.30	6.10
5.08	10.20	5.20	8.80	5.40	6.50
5.10	10.45	5.30	9.05	5.60	7.25
		5.40	9.20	5.80	7.85
		5.60	9.45	5.90	8.15
		5.80	9.65		

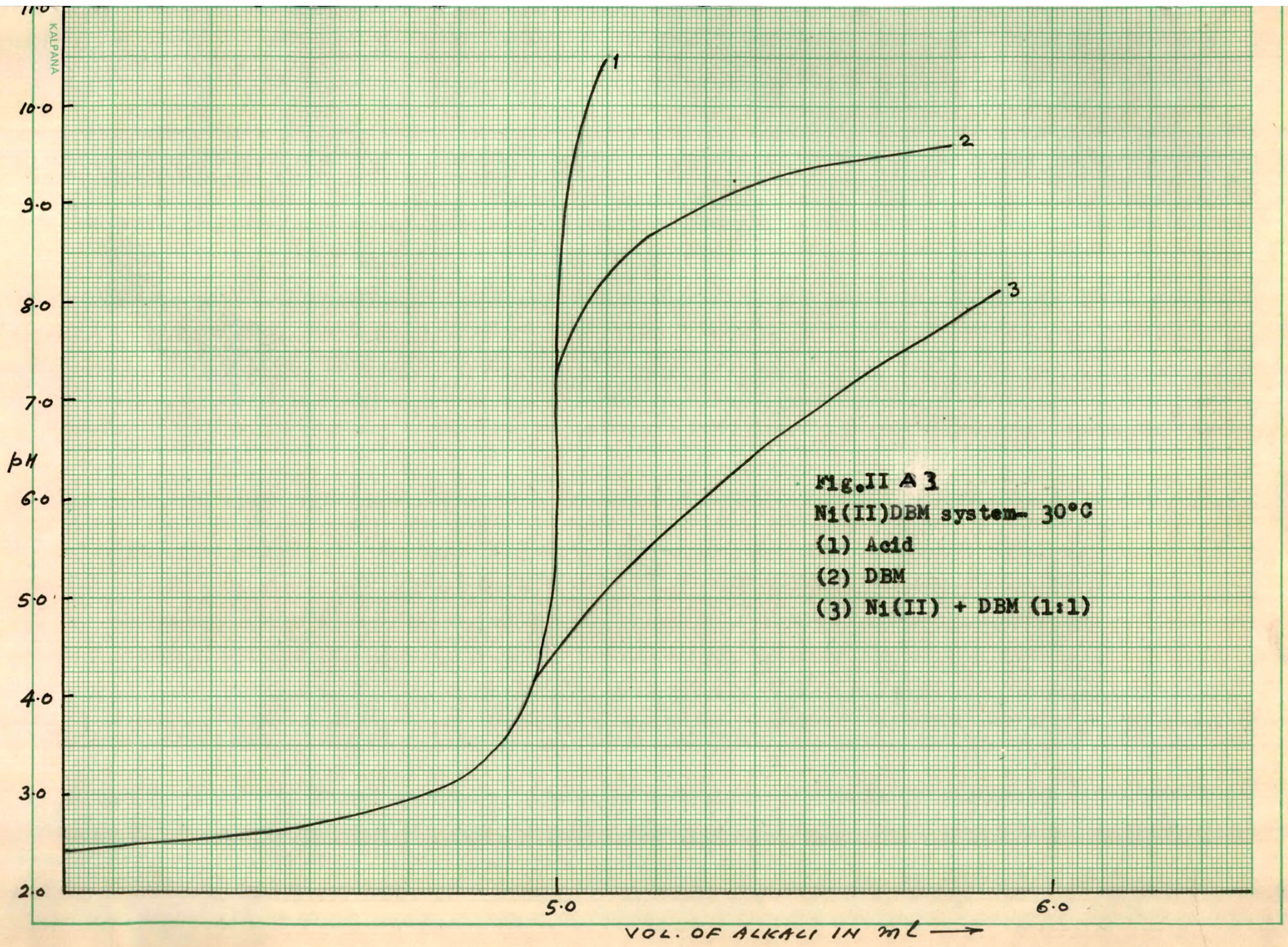


Fig.II A 3

Ni(II)DBM system- 30°C

(1) Acid

(2) DBM

(3) Ni(II) + DBM (1:1)

Table II A 2.1a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Cu(II) acetylacetone system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.50	1.00_0	4.89	5.12	0.23	0.46_1	0.06_9	9.21_9	9.15_0
3.55	1.00_0	4.90	5.14	0.24	0.48_0	0.03_5	9.18_6	9.15_1
3.60	1.00_0	4.91	5.16	0.25	0.50_0	-	9.15_3	9.15_3
3.65	1.00_0	4.92	5.17	0.25	0.50_0	-	9.10_3	9.10_3
3.70	1.00_0	4.93	5.19	0.26	0.52_0	$\bar{1}.96_5$	9.07_1	9.10_6

$\log K_1 = 9.13 \pm 0.01$

Table II A 2.2a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Cu(II) benzoylacetone system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.35	1.00_0	4.86	5.07	0.21	0.42_1	0.13_8	9.47_8	9.34_0
3.40	1.00_0	4.88	5.12	0.24	0.48_1	0.03_3	9.47_6	9.44_3
3.45	1.00_0	4.89	5.16	0.27	0.54_1	$\bar{1}.92_9$	9.49_7	9.55_0
3.50	1.00_0	4.90	5.19	0.29	0.58_1	$\bar{1}.85_6$	9.46_9	9.61_3
3.55	1.00_0	4.91	5.20	0.29	0.58_1	$\bar{1}.85_6$	9.41_9	9.56_3

$\log K_1 = 9.50 \pm 0.06$

Fig.II A 4

Cu(II) AcAc system - 30°C.

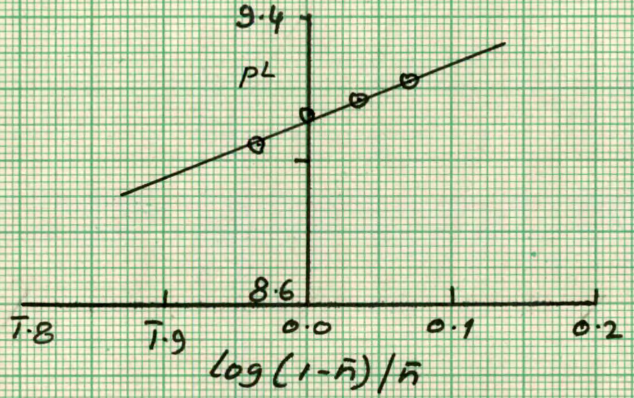


Fig.II A 5

Cu(II) BA system - 30°C

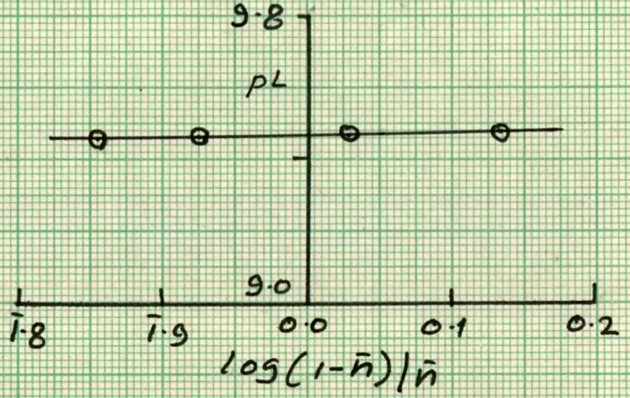


Table II A 2.3b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni(II) acetylacetone system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.95	1.00_0	5.00	5.21	0.21	0.42_0	0.14_0	6.73_9	6.59_9
6.00	1.00_0	5.00	5.22	0.22	0.44_0	0.10_5	6.70_4	6.59_9
6.05	1.00_0	5.00	5.23	0.23	0.46_0	0.06_9	6.66_9	6.60_0
6.10	1.00_0	5.00	5.25	0.25	0.50_0	-	6.65_3	6.65_3
6.15	1.00_0	5.00	5.26	0.26	0.52_0	$\bar{1}.96_5$	6.62_1	6.65_6
6.20	1.00_0	5.00	5.27	0.27	0.54_0	$\bar{1}.93_5$	6.58_9	6.65_4
6.25	1.00_0	5.00	5.29	0.29	0.58_0	$\bar{1}.85_9$	6.57_9	6.72_0

$\log K_1 = 6.64 \pm 0.02$

Table II A 2.4b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni(II) benzoylacetone system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.85	1.00_0	5.00	5.21	0.21	0.42_0	0.14_0	6.97_9	6.83_9
5.90	1.00_0	5.00	5.22	0.22	0.44_0	0.10_5	6.94_4	6.83_9
5.95	1.00_0	5.00	5.23	0.23	0.46_0	0.06_9	6.90_9	6.84_0
6.00	1.00_0	5.00	5.24	0.24	0.48_0	0.03_5	6.87_6	6.84_1
6.05	1.00_0	5.00	5.25	0.25	0.50_0	-	6.84_3	6.84_3
6.10	1.00_0	5.00	5.26	0.26	0.52_0	$\bar{1}.96_5$	6.81_1	6.84_6
6.15	1.00_0	5.00	5.27	0.27	0.54_0	$\bar{1}.93_5$	6.77_9	6.84_4

$\log K_1 = 6.84 \pm 0.01$

Table II A 2.5b

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data for Ni(II) dibenzoylmethane system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
5.65	1.00_0	5.00	5.21	0.21	0.42_0	0.14_0	7.39_9	7.25_9
5.70	1.00_0	5.00	5.22	0.22	0.44_0	0.10_5	7.36_4	7.25_9
5.75	1.00_0	5.00	5.23	0.23	0.46_0	0.06_9	7.32_9	7.26_2
5.80	1.00_0	5.00	5.24	0.24	0.48_0	0.03_5	7.29_6	7.26_1
5.85	1.00_0	5.00	5.25	0.25	0.50_0	-	7.26_3	7.26_3
5.90	1.00_0	5.00	5.26	0.26	0.52_0	$\bar{1}.96_5$	7.23_1	7.26_6
5.95	1.00_0	5.00	5.27	0.27	0.54_0	$\bar{1}.93_5$	7.19_9	7.26_4

$\log K_1 = 7.26 \pm 0.01$

Fig. II A 6
Ni(II) AcAc system - 30°C.

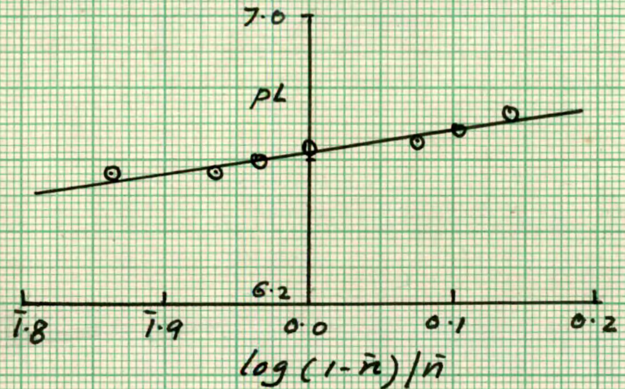


Fig.II A 7
Ni(II) BA system - 30°C.

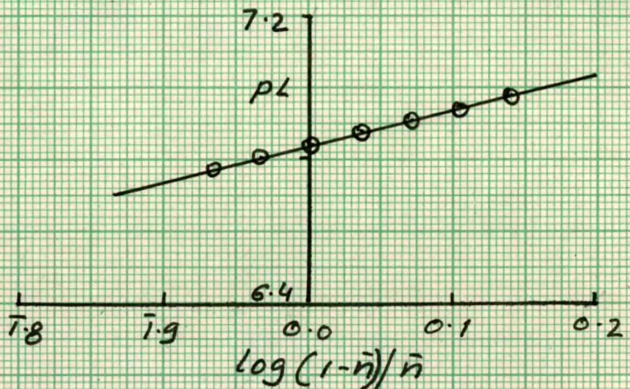


Fig.II A 8
Ni(II) DBM system - 30°C.

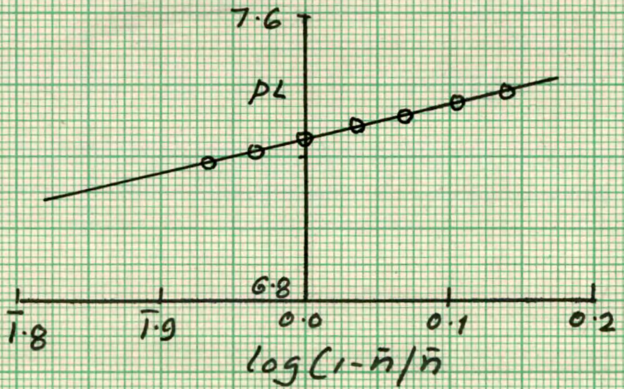


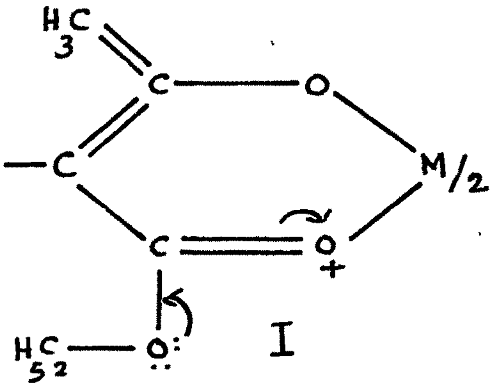
Table II A-3.0 : Proton and metal ligand stability constants of β-diketones - 30°C.

Ligand	$P_{K_1}^{H}$	$\log K_1$ Cu(II)	$\log K_1$ Ni(II)
Acetylacetone	9.71	9.13 ± 0.01	6.64 ± 0.02
Benzoylacetone	9.85	9.50 ± 0.06	6.84 ± 0.01
Dibenzoylmethane	10.07	-	7.26 ± 0.01

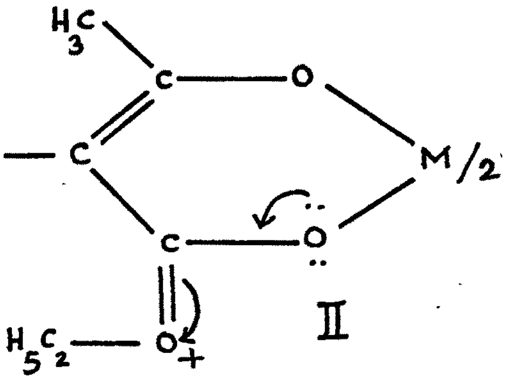
Section B :

As seen in the earlier section, the β-diketones form very stable complexes, due to formation of a six membered planar ring, with delocalised π electrons, on coordination to a metal ion.

When an -OR group is substituted for one of the R groups in β-diketone, thereby producing an acetoacetic ester, the metal ligand formation constants are lowered considerably as compared to the diketones and this has been attributed to the fact that the resonance in the chelate ring of the diketone is greatly interfered with by the participation of one of the carbonyl groups in the very strong ester resonance.[4]



I



II

Formation constants of ethylacetoacetates of rare earths have been reported by Dutt and coworkers.[17] They have also determined formation constants of ethyl-thioacetate complexes of rare earths potentiometrically.[18] Formation constants of lanthanide chelates of ethylbenzoylacetate, have been studied potentiometrically, and the existance of 1:1 chelate has been shown in solution.[19] Acid dissociation constants of β-ketoesters and the stability constants of their divalent transition metals and dioxouranium (II) chelates have been determined potentiometrically[20] in 75% volume dioxan water medium. The ligands used in these studies have the general formula $RCOCHR'COEt$ ($R = Me$, $R' = H$, Ph; $R = PhCH_2$, $R' = Ph$; $R = Phc{:}c$, $R' = Ph$, α-naphthyl).

The studies of complexes of acetoacetic esters with substitution at the third carbon atom have not been carried out earlier. This may throw some light on the extent of π interaction in β-ketoester complexes. In the present investigation, studies of binary metal β-ketoester complexes have been carried out using Irving-Rossotti method[11] ; where M = Cu(II), Ni(II), Zn(II) or Be(II). The ligands are ethylacetoacetate, ethyl-2-methylacetoacetate; ethyl-2-ethylacetoacetate, ethyl-2-propylacetoacetate, ethyl-2-isopropylacetoacetate, ethyl-2-butylacetoacetate.

Experimental :

The alkyl substituted ligands used were all of pure grade (Fluka, A.R.). Solution of zinc perchlorate was prepared as in case of nickel perchlorate in previous section. Beryllium nitrate was used due to non availability of pure quality of beryllium carbonate, necessary for the preparation of perchlorate. Other chemicals used were same as in chapter II section A. The instruments used and the titrations carried out are same as in section A of this chapter. Titrations were carried out in 50% water dioxan medium and the pH corrections were made as before. In all three sets were prepared as follows :

1. Acid titration :

   0.02M $HClO_4$, 0.178M $NaClO_4$

2. Reagent titration :

   0.02M $HClO_4$, 0.01M ligand and 0.177M $NaClO_4$.

3. Metal titration :

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

The ratio of 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. The titration data and curves are given in tables II B 1.1 to II B 1.9 and figs. II B 1 to II B 9, respectively.

Determination of proton ligand and metal ligand stability constants :

It is seen in the Irving-Rossotti titration curves (figs. II B 1 to II B 9) that in the lower pH range the acid and the ligand curves 1 and 2 overlap each other. In the higher pH range, however, the ligand curve exhibits lower values of pH than the acid titration curve showing presence of more number of titratable H^+ ions due to dissociation of the H^+ of enolic -OH. It is due to the liberation of the H^+ ions that the ligand has extra titratable H^+ ions.

$\bar{n}_H$ and proton ligand stability constants were calculated using equations described in chapter II section A. However, it is found that $\log k_1/\log k_2 < 10^{2.5}$ and hence the linear plot method is not applicable. In such cases it is best to calculate the formation constant using least square technique.

In cases of systems with ML_2 as the highest complex,

$$\bar{n} + (\bar{n}-1)k_1[L] + (\bar{n}-2)k_1.k_2[L]^2 = 0 \qquad (2.6)$$

The above equation may be rearranged as follows :

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})[L]}{(\bar{n}-1)} \cdot \beta_2 - k_1 \qquad (2.7)$$

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 $\bar{n} / (\bar{n}-1)[L]$ vs $(2-\bar{n})[L]/(\bar{n}-1)$.

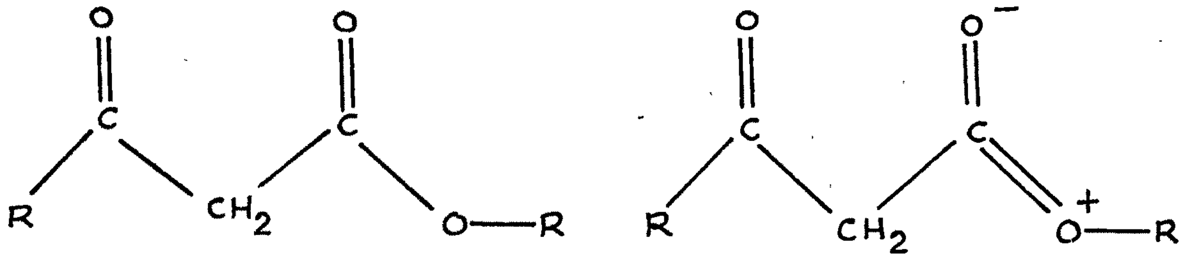
Therefore, the constants $\beta_2(k_1.k_2)$ and k_1 are best evaluated by the method of least square. It makes use of all the experimental points except those between $\bar{n} = 0.95$ and 1.05 (which, for this purpose, are too sensitive to slight experimental errors), In this method firstly the values 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 summated over all number of points taken to give ΣY and ΣX, respectively. Next values of X^2 and XY were tabulated and added to gave ΣX^2 and ΣXY, respectively. These sums were used to solve standard simultaneous equations for the least square which are,

$$\Sigma Y = k.a_0 + a_1 \Sigma X.$$
$$\Sigma XY = a_0.\Sigma X + A_1 \Sigma X^2. \qquad (2.8)$$

where k is equal to the number of observations, the coefficient a_0 is $-k_1$ and a_1 is β_2. The solution of equation (2.8) gave mean value for $\log k_2$. Further the mean value of k_1 was fitted into equation (2.7) and then values of β_2 were determined at different pH values. Similarly values of k_1 was determined at each point by using the average values of β_2. The value of k_1 and β_2 at each point have been summed up to get the average value. The deviation of each point from the average value was calculated. These were summed up to get the mean deviation. The calculations and precise values of first and second formation constants obtained by this method have been tabulated in tables II B 2.1a' to II B 5.3d'.

The average values of logk$_1$ and logk$_2$ with mean deviation obtained by least square or linear plot method have been represented in tables II B 6.0.

The β-ketoesters are characterised by one P_K^H value. The value is however higher by one log unit as compared to the diketones. The keto enol tautomer exists in the β-ketoesters but the enol content is very much reduced. This can be attributed largely to a cross conjugation between the ester group and the enol structure.



The resonance of the ester group occurs at the expense of the resonance of the enol ring[8]. This destabilises the enol with respect to the keto tautomer and shifts the equilibrium towards the ketone, so much so that its K_H value is raised by $\sim$ 1 log unit.

In case of β-diketones it is known[21] that substitution of hydrogen over carbon by an alkyl group increases the basicity of the ligand. This is due to the positive inductive effect of the alkyl group and also the distortion of the ring resulting in lowering of resonance and hence the enol form. Thus C-methylacetylacetone is more basic than acetylacetone.

However, it forms less stable complexes. The lowering in value of formation constants can also be explained to be due to the lowering in the resonance of the chelate ring. This may be because of the steric hindrance between the methyl groups, distorting the planarity of the ring and thus reducing the resonance.

With bulkier groups at the C-carbon atom the steric effect will distort the structure further from planarity, thus reducing resonance further, and hence there is lowering in the value of formation constants. The lowering in the formation constant values with substitution at the C-carbon atom supports the resonance stabilisation of the β-diketone complexes.

Proton ligand stability constants and metal ligand formation constants of C-alkyl substituted acetoacetic ester complexes compared to unsubstituted acetoacetic ester may throw some light on the extent of πointeraction in the β-keto-esters.

In case of C-methyl acetoacetic ester the steric hindrance between the $C-CH_3$ and the $-OC_2H_5$ group is expected to be more than in case of C-substituted acetylacetone. Thus the difference in the proton ligand formation constant values in case of acetoacetic ester and C-methyl derivative should be more than in acetylacetone and C-methyl acetylacetone. However, in case of C-alkyl substituted acetoacetic ester the increase in basicity is not so much as in the case of β-diketones. As stated earlier the increase in basicity of the β-diketones, is due to inductive effect as well as ring distortion effect lowering the enol form. In case of β-ketoesters however, the enol form is already very much reduced and hence lowering in enol form due to the distortion in the ring does not have significant effect. The small increase in basicity may be mainly due to the inductive effect of the alkyl group. This is the reason why there is a small difference in the proton ligand stability constant values of the different β-ketoesters.

In the β-ketoester complexes it is observed that there is very little difference in the formation constant values of the ethylacetoacetate complexes and that of C-methyl substituted compounds. If resonance stabilisation of the chelate ring would have had a significant contribution in determining the formation constant values of the β-ketoester compound, the distortion in planarity due to substitution at C-atom should have lowered the formation constant values significantly. There should have been a significant difference in the formation constants of the β-ketoester complexes and the C-alkyl substituted derivative.

However, the formation constant data, shows that the distortion in planarity of the ring due to substitution on the C-atom does not affect the values of formation constants significantly; in case of β-ketoester complexes.

Thus it can be inferred that the contribution due to resonance, in the chelate ring of β-ketoesters is much less. This is an evidence in support of the fact that the π interaction in acetoacetic ester is much less than in the β-diketone complexes.

Table II B 1.1

$N = 0.2M$ $V^\circ = 50$ ml. $T^\circ_L = 0.01M$ $T^\circ_M = 0.001M$

$E^\circ = 0.02M$ $\mu = 0.2M$ $t = 30^\circ C.$

Perchloric acid		Ethylaceto-acetate		Cu(II)		Ni(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.95	3.90	4.95	4.05
4.94	3.85	4.98	4.60	5.00	4.05	5.00	5.25
4.96	4.15	5.00	6.95	5.05	4.25	5.05	5.75
4.98	4.60	5.05	7.70	5.10	4.40	5.10	6.00
5.00	7.20	5.10	8.20	5.20	4.90	5.20	6.45
5.01	8.50	5.20	9.00	5.30	5.45	5.30	6.85
5.05	9.55	5.30	9.70	5.40	5.95	5.40	7.20
5.08	10.20	5.40	10.25	5.60	7.65	5.60	8.65
5.10	10.45	5.50	10.70	5.80	9.85	5.80	10.55
				5.90	10.50		

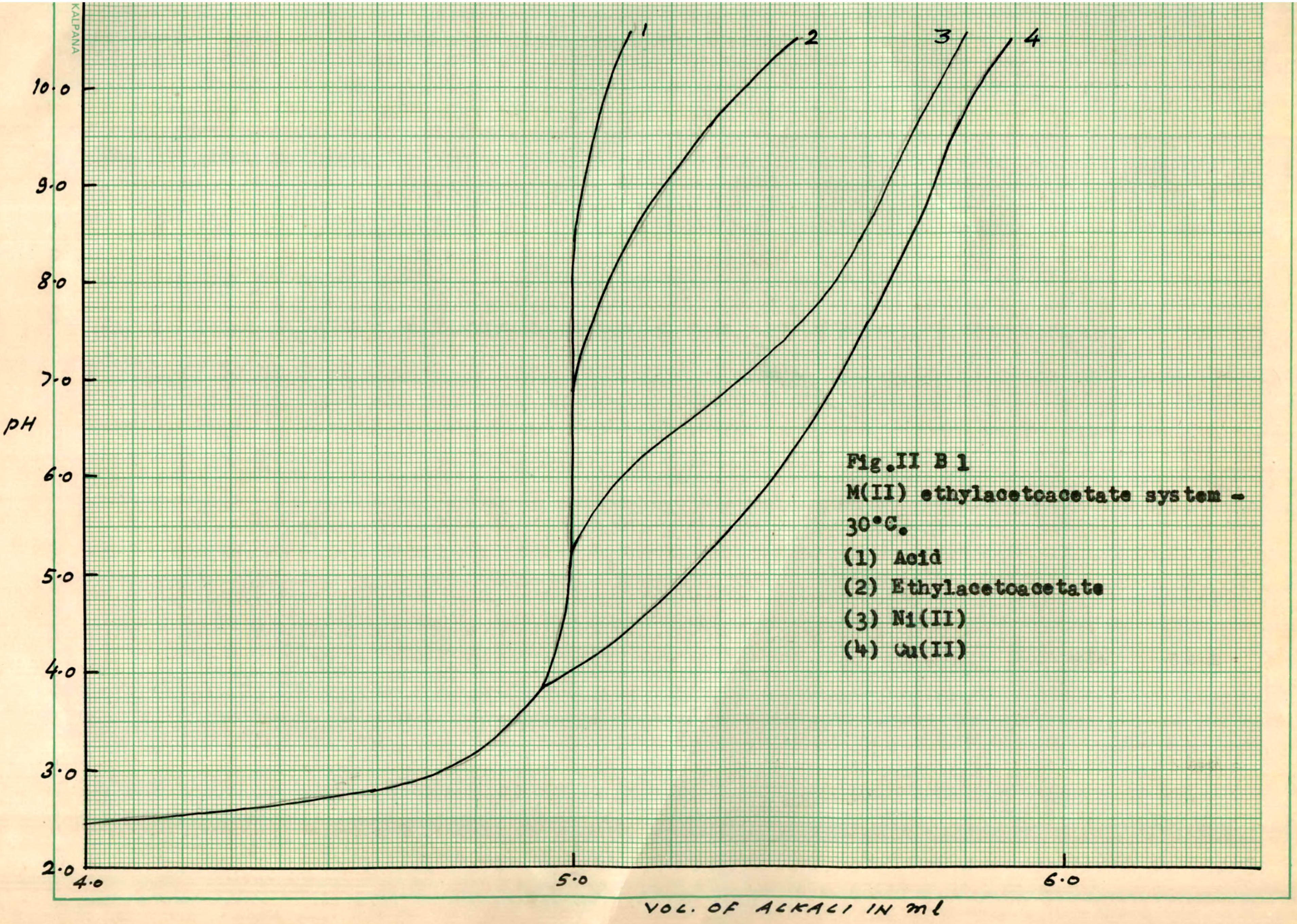


Fig.II B 1
M(II) ethylacetoacetate system -
30°C.
(1) Acid
(2) Ethylacetoacetate
(3) Ni(II)
(4) Cu(II)

Table IIB 1.2

N = 0.2M V° = 50 ml. T_L° = 0.01M T_M° = 0.001M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		Ethylaceto-acetate		Zn(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.90	3.55	4.90	3.55
4.90	3.55	4.90	3.55	4.95	4.00	4.95	4.00
4.92	3.65	4.94	3.85	5.00	5.45	5.00	6.00
4.94	3.85	4.98	4.60	5.05	6.00	5.05	6.70
4.96	4.15	5.00	6.95	5.10	6.25	5.10	6.95
4.98	4.60	5.05	7.70	5.20	6.65	5.20	7.40
5.00	7.20	5.10	8.20	5.30	7.00	5.30	8.20
5.01	8.50	5.20	9.00	5.40	7.35	5.40	9.50
5.05	9.55	5.30	9.70	5.60	8.05	5.50	10.00
5.08	10.00	5.40	10.25	5.80	10.50	5.60	10.50
5.10	10.45	5.50	10.70				

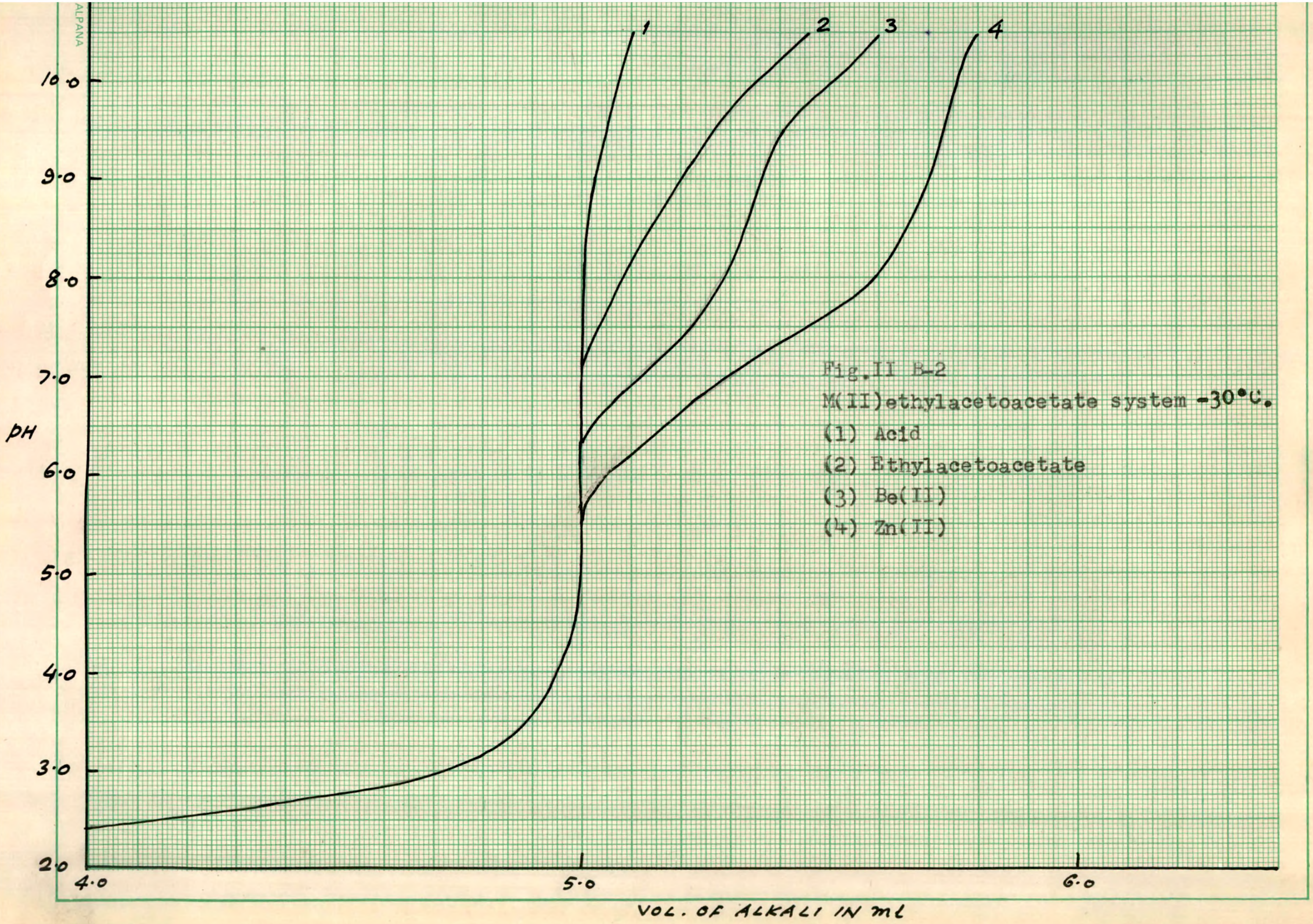


Fig.II B-2

M(II)ethylacetoacetate system -30°C.

(1) Acid

(2) Ethylacetoacetate

(3) Be(II)

(4) Zn(II)

Table IIB 1.3

$N = 0.2M$ $V^{\circ} = 50$ ml. $T_L^{\circ} = 0.01M$ $T_M^{\circ} = 0.001M$

$E^{\circ} = 0.02M$ $\mu = 0.2M$ $t = 30^{\circ}C.$

Perchloric acid		Ethyl-2-methyl acetoacetate		Cu(II)		Ni(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.95	4.10	4.95	4.10
4.94	3.85	4.98	4.60	5.00	4.20	5.00	5.45
4.96	4.15	5.00	6.95	5.05	4.40	5.05	6.00
4.98	4.60	5.05	7.15	5.10	4.55	5.10	6.35
5.00	7.20	5.10	8.20	5.15	4.75	5.20	6.75
5.01	8.50	5.15	8.80	5.20	4.95	5.30	7.05
5.05	9.55	5.20	9.25	5.30	5.55	5.40	7.30
5.08	10.20	5.25	9.75	5.40	6.15	5.50	7.60
5.10	10.45	5.30	10.15	5.60	7.80	5.60	8.05
		5.35	10.50	5.80	9.70	5.80	10.40
				5.90	10.45		

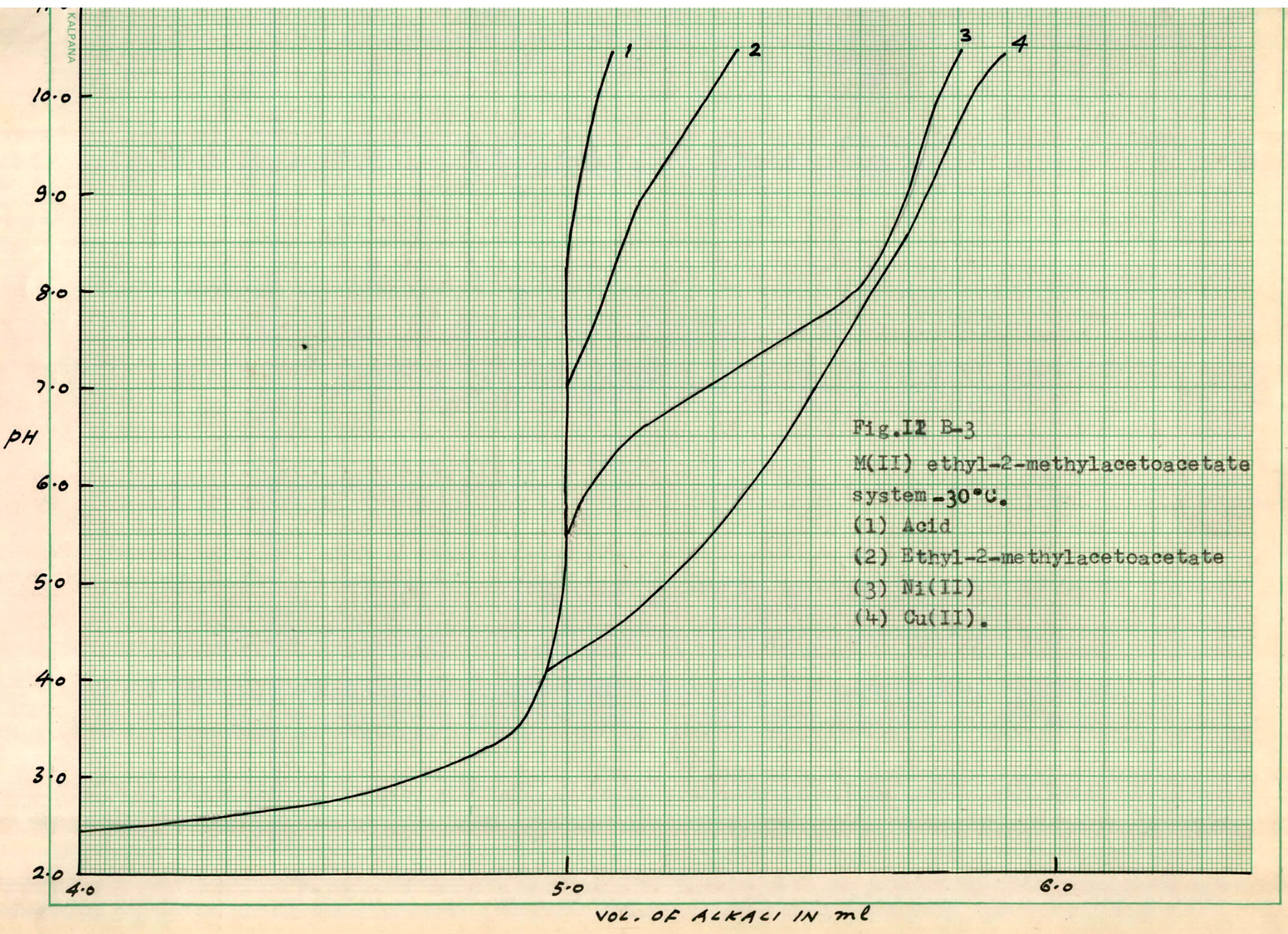


Fig.12 B-3

M(II) ethyl-2-methylacetoacetate system -30°C.

(1) Acid

(2) Ethyl-2-methylacetoacetate

(3) Ni(II)

(4) Cu(II).

Table IIB 1.4

$N = 0.2M$ $V^\circ = 50$ ml. $T_L^\circ = 0.01M$ $T_M^\circ = 0.001M$

$E^\circ = 0.02M$ $\mu = 0.2M$ $t = 30°C.$

Perchloric acid		Ethyl-2-methyl acetoacetate		Zn(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.94	3.85	4.94	3.85
4.94	3.85	4.98	4.60	4.98	4.60	4.98	4.60
4.96	4.15	5.00	6.95	5.00	5.75	5.00	6.20
4.98	4.60	5.05	7.15	5.05	6.25	5.05	6.65
5.00	7.20	5.10	8.20	5.10	6.55	5.10	7.00
5.01	8.50	5.15	8.80	5.15	6.75	5.15	7.25
5.05	9.55	5.20	9.25	5.20	6.90	5.20	7.45
5.08	10.20	5.25	9.75	5.30	7.20	5.30	8.35
5.10	10.45	5.30	10.15	5.40	7.50	5.40	9.70
		5.35	10.50	5.60	8.05	5.50	10.50
				5.80	10.50		

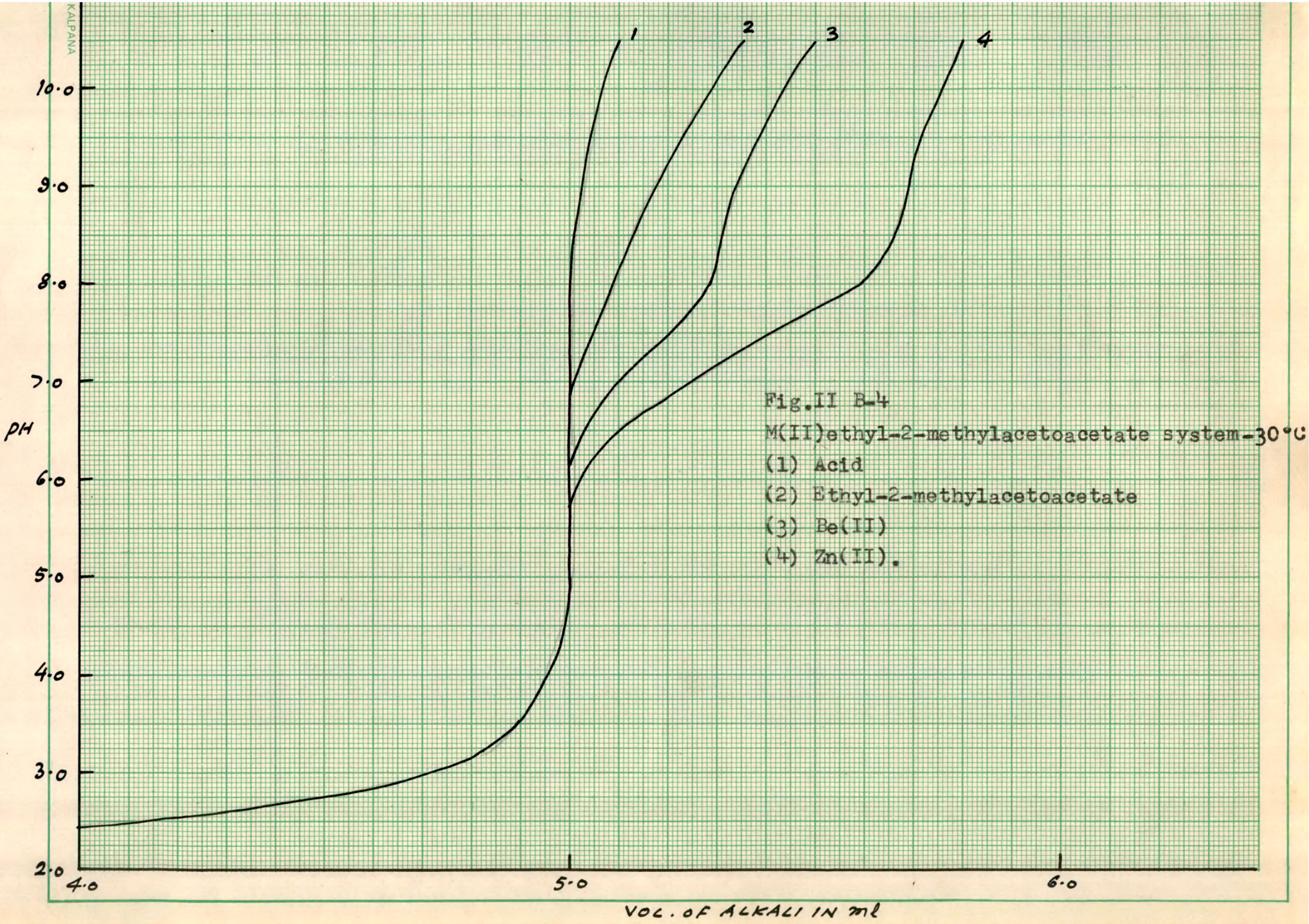


Fig.II B-4
M(II)ethyl-2-methylacetoacetate system-30°C
(1) Acid
(2) Ethyl-2-methylacetoacetate
(3) Be(II)
(4) Zn(II).

Table IIB 1.5

N = 0.2M V° = 50 ml. T_L° = 0.01M T_M° = 0.001M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		Ethyl-2-ethyl acetoacetate		Cu(II)		Ni(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.95	3.95	4.95	3.95
4.94	3.85	4.98	4.60	5.00	4.15	5.00	5.75
4.96	4.15	5.00	7.05	5.05	4.35	5.05	6.20
4.98	4.60	5.05	7.75	5.10	4.60	5.10	6.50
5.00	7.20	5.10	8.45	5.20	5.10	5.20	6.90
5.01	8.50	5.15	9.00	5.30	5.60	5.30	7.25
5.05	9.55	5.20	9.50	5.40	6.25	5.40	7.45
5.08	10.20	5.25	9.95	5.60	7.80	5.50	7.75
5.10	10.45	5.30	10.30	5.80	9.65	5.70	9.10
		5.35	10.60	6.00	10.70	5.90	10.75

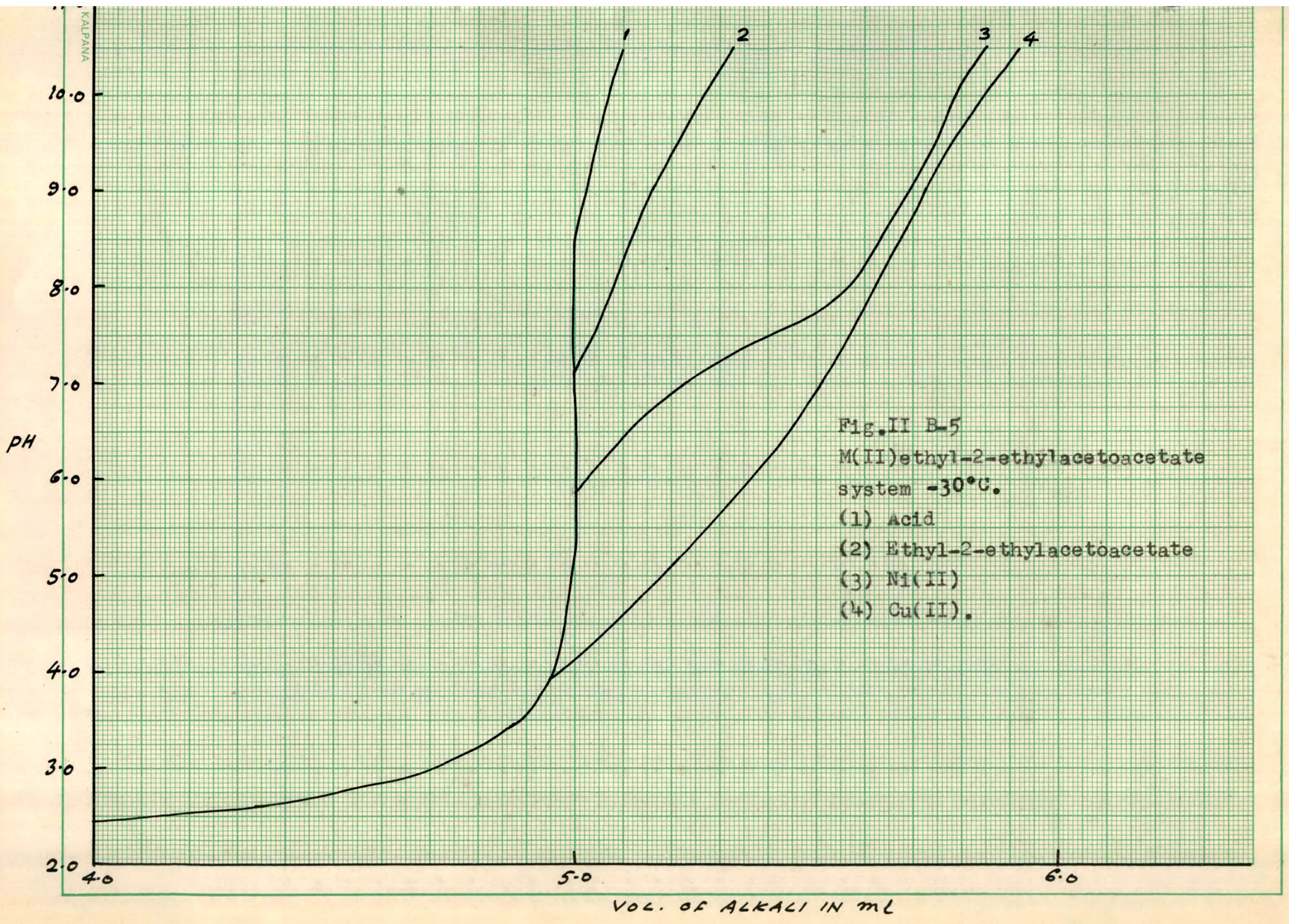


Fig.II B-5
M(II)ethyl-2-ethylacetoacetate
system -30°C.
(1) Acid
(2) Ethyl-2-ethylacetoacetate
(3) Ni(II)
(4) Cu(II).

Table IIB 1.6

N = 0.2M V° = 50 ml. T_L° = 0.01M T_M° = 0.001M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		Ethyl-2-ethyl acetoacetate		Zn(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	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.94	3.85	4.94	3.85
4.94	3.85	4.98	4.60	4.98	4.60	4.98	4.60
4.96	4.15	5.00	7.05	5.00	5.90	5.00	6.25
4.98	4.60	5.05	7.75	5.05	6.50	5.05	6.85
5.00	7.20	5.10	8.45	5.10	6.80	5.10	7.20
5.01	8.50	5.15	9.00	5.15	7.00	5.15	7.50
5.05	9.55	5.20	9.50	5.20	7.20	5.20	7.70
5.08	10.20	5.25	9.95	5.30	7.45	5.30	8.50
5.10	10.45	5.30	10.30	5.40	7.70	5.40	9.75
		5.35	10.60	5.60	8.50	5.50	10.50
				5.80	10.50		

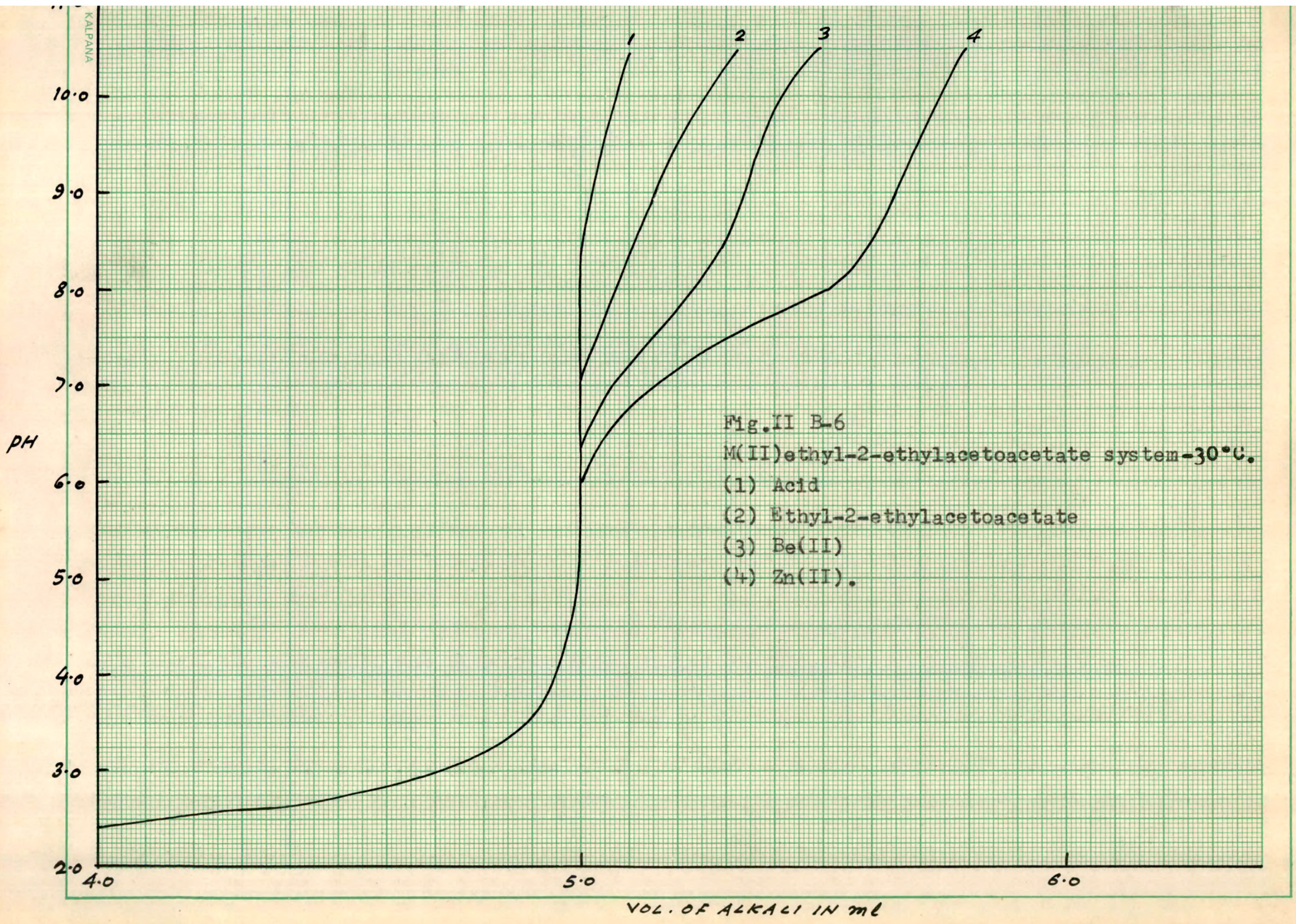


Fig.II B-6

M(II)ethyl-2-ethylacetoacetate system-30°C.

(1) Acid

(2) Ethyl-2-ethylacetoacetate

(3) Be(II)

(4) Zn(II).

Table IIB 1.7

N = 0.2M   V° = 50 ml. T_L° = 0.01M T_M° = 0.001M

E° = 0.02M μ = 0.2M   t = 30°C.

Perchloric acid		Ethyl-2-propyl-acetoacetate		Cu(II)		Ni(II)		Zn(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	Vol.of alkali (in ml.)	B
0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.95	4.00	4.95	4.00	4.95	4.00
4.94	3.85	4.98	4.60	5.00	4.25	5.00	6.00	5.00	6.25
4.98	4.60	5.00	7.15	5.05	4.45	5.05	6.75	5.05	6.85
5.00	7.20	5.05	8.10	5.10	4.70	5.10	7.00	5.10	7.15
5.01	8.50	5.10	8.70	5.20	5.20	5.20	7.50	5.20	7.60
5.05	9.55	5.15	9.20	5.30	5.75	5.30	7.70	5.30	7.80
5.08	10.20	5.20	9.65	5.40	6.35	5.40	7.95	5.40	8.05
5.10	10.45	5.25	10.15	5.60	8.60	5.50	8.40	5.50	8.50
		5.30	10.60	5.80	10.40	5.70	10.50	5.60	10.00

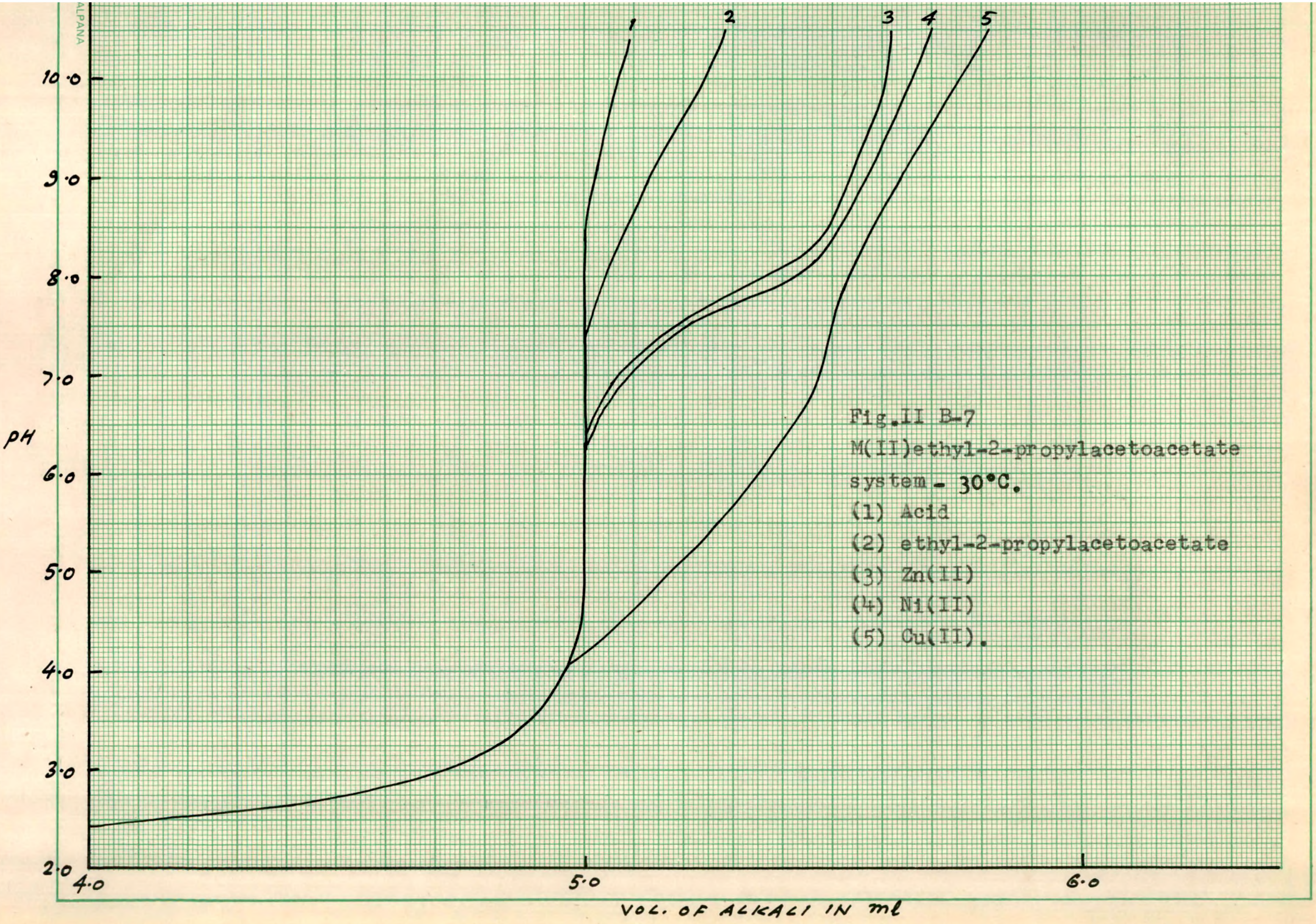


Fig.II B-7
M(II)ethyl-2-propylacetoacetate
system - 30°C.
(1) Acid
(2) ethyl-2-propylacetoacetate
(3) Zn(II)
(4) Ni(II)
(5) Cu(II).

Table IIB 1.8

$N = 0.2M$ $V^{\circ} = 50$ ml. $T_L^{\circ} = 0.01M$ $T_M^{\circ} = 0.001M$

$E^{\circ} = 0.02M$ $\mu = 0.2M$ $t = 30^{\circ}C.$

Perchloric acid		Ethyl-2-iso-propyl-acetoacetate		Cu(II)		Ni(II)		Zn(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	Vol.of alkali (in ml.)	B
0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.95	4.00	4.95	4.00	4.95	4.00
4.94	3.85	4.98	4.60	5.00	4.25	5.00	6.15	5.00	6.25
4.96	4.15	5.00	7.25	5.05	4.45	5.05	6.70	5.05	6.80
4.98	4.60	5.05	8.05	5.10	4.70	5.10	7.00	5.10	7.05
5.00	7.20	5.10	8.65	5.20	5.25	5.20	7.35	5.20	7.45
5.01	8.50	5.15	9.25	5.30	5.75	5.30	7.60	5.30	7.70
5.05	9.55	5.20	9.75	5.40	6.30	5.40	7.85	5.40	7.95
5.08	10.20	5.25	10.20	5.60	8.25	5.60	9.00	5.60	9.50
5.10	10.45	5.30	10.60	5.80	10.60	5.70	10.20	5.70	10.65

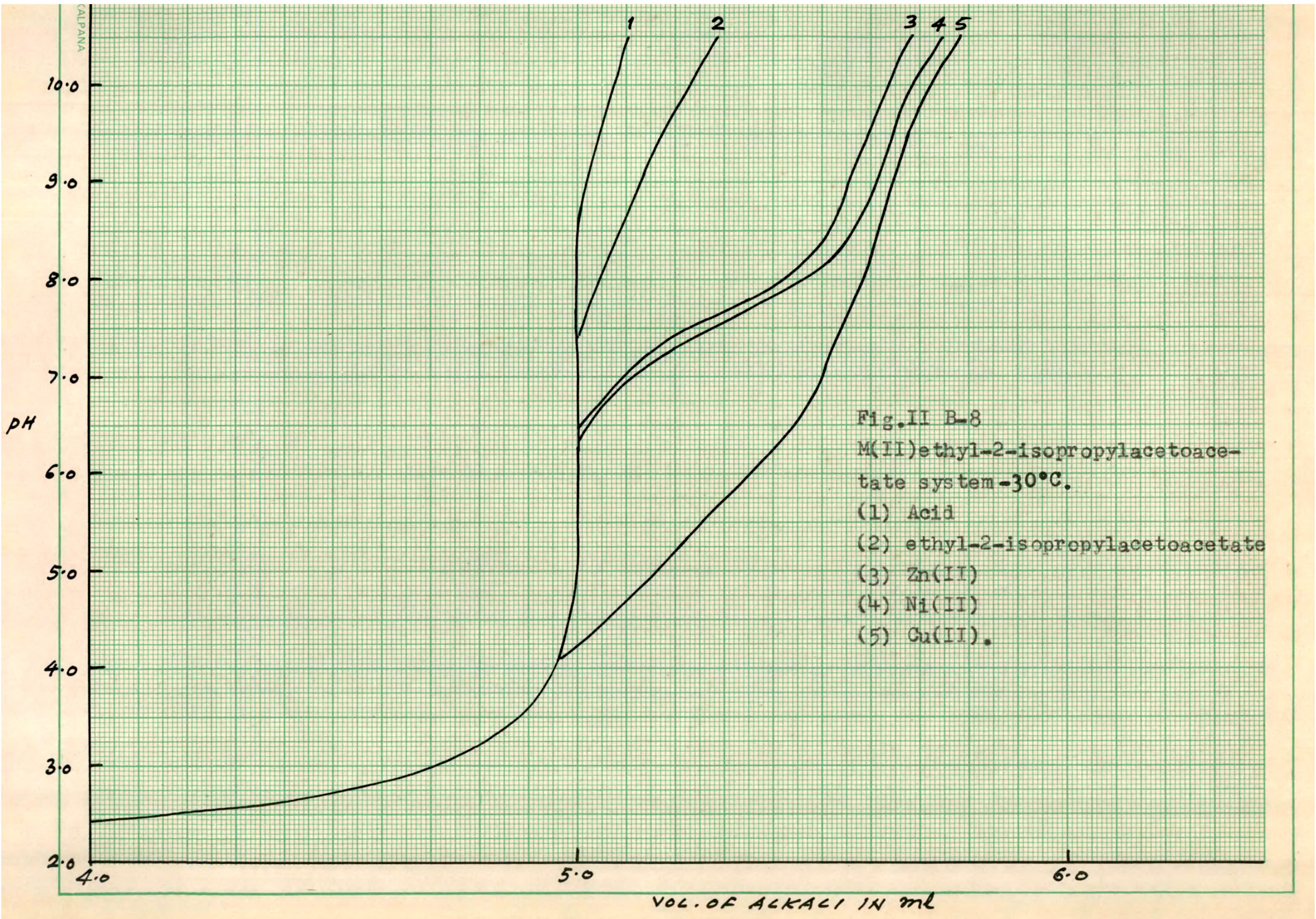


Fig.II B-8
M(II)ethyl-2-isopropylacetoacetate system -30°C.
(1) Acid
(2) ethyl-2-isopropylacetoacetate
(3) Zn(II)
(4) Ni(II)
(5) Cu(II).

Table IIB 1.9

N = 0.2M   V° = 50 ml. T_L° = 0.01M T_M° = 0.001M

E° = 0.02M μ = 0.2M   t = 30°C.

Perchloric acid		Ethyl-2-butyl-acetoacetate		Cu(II)		Ni(II)		Zn(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	Vol.of alkali (in ml.)	B
0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80	0.00	1.80
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15	3.00	2.15
4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45	4.00	2.45
4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75	4.50	2.75
4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85	4.60	2.85
4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00	4.70	3.00
4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20	4.80	3.20
4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35	4.85	3.35
4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55	4.90	3.55
4.92	3.65	4.94	3.85	4.95	4.00	4.95	4.00	4.95	4.00
4.94	3.85	4.98	4.60	5.00	4.50	5.00	6.25	5.00	6.50
4.96	4.15	5.00	7.15	5.05	4.75	5.05	6.85	5.05	7.10
4.98	4.60	5.05	7.90	5.10	4.95	5.10	7.15	5.10	7.35
5.00	7.20	5.10	8.50	5.20	5.40	5.20	7.50	5.20	7.70
5.01	8.50	5.15	9.25	5.30	5.90	5.30	7.75	5.30	7.95
5.05	9.55	5.20	9.90	5.40	6.70	5.40	8.00	5.40	8.20
5.08	10.20	5.25	10.45	5.50	7.30	5.50	8.25	5.50	8.70
5.10	10.45			5.70	10.00	5.70	10.60	5.60	10.25

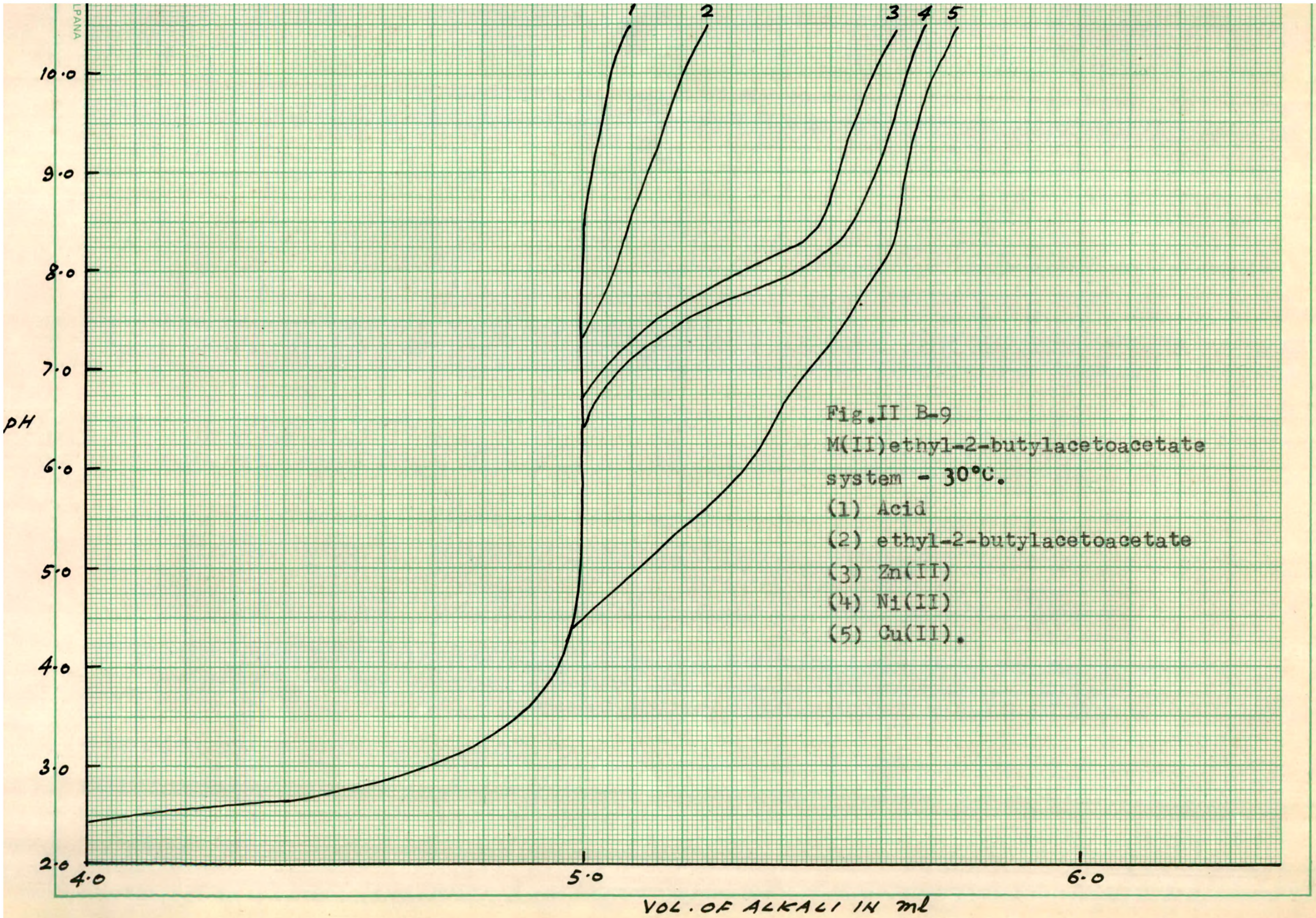


Fig.II B-9
M(II)ethyl-2-butylacetoacetate
system - 30°C.
(1) Acid
(2) ethyl-2-butylacetoacetate
(3) Zn(II)
(4) Ni(II)
(5) Cu(II).

Table II B 2.1a

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

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
4.35	1.00_0	4.97	5.09	0.12	0.48_0	8.86_2
4.40	1.00_0	4.97	5.10	0.13	0.52_0	8.81_4
4.45	1.00_0	4.97	5.11	0.14	0.56_0	8.76_6
4.50	1.00_0	4.89	5.13	0.15	0.60_0	8.71_9
4.55	1.00_0	4.98	5.14	0.16	0.64_0	8.67_1
4.60	1.00_0	4.98	5.15	0.17	0.68_0	8.62_3
5.55	1.00_0	5.00	5.33	0.33	1.32_0	7.65_6
5.60	1.00_0	5.00	5.34	0.34	1.36_0	7.60_8
5.65	1.00_0	5.00	5.35	0.35	1.40_0	7.56_0
5.70	1.00_0	5.00	5.36	0.36	1.44_0	7.51_2
5.75	1.00_0	5.00	5.37	0.37	1.48_0	7.46_4

Table II B 2.2a

$\bar{n}_H$, $\bar{n}$, pL data for Cu(II) ethyl-2-methylacetoacetate system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"' - V"	$\bar{n}$	pL
4.55	1.00_0	4.98	5.10	0.12	0.48_0	8.76_0
4.60	1.00_0	4.98	5.11	0.13	0.52_0	8.71_2
4.65	1.00_0	4.99	5.13	0.14	0.56_0	8.67_0
4.70	1.00_0	4.99	5.14	0.15	0.60_0	8.62_3
4.75	1.00_0	4.99	5.15	0.16	0.64_0	8.57_5
4.80	1.00_0	4.99	5.16	0.17	0.68_0	8.52_7
5.75	1.00_0	5.00	5.33	0.33	1.32_0	7.60_9
5.80	1.00_0	5.00	5.34	0.34	1.36_0	7.56_1
5.85	1.00_0	5.00	5.35	0.35	1.40_0	7.51_3
5.90	1.00_0	5.00	5.36	0.36	1.44_0	7.46_5
5.95	1.00_0	5.00	5.37	0.37	1.48_0	7.41_7

Table II B 2.3a

$\bar{n}_H$, $\bar{n}$, pL data for Cu(II) ethyl-2-ethylacetoacetate system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.80	1.00_0	4.99	5.13	0.14	0.56_0	8.55_2
4.85	1.00_0	4.99	5.14	0.15	0.60_0	8.50_4
4.90	1.00_0	4.99	5.15	0.16	0.64_0	8.45_6
4.95	1.00_0	4.99	5.16	0.17	0.68_0	8.40_8
6.05	1.00_0	5.00	5.36	0.36	1.44_0	7.34_7
6.10	1.00_0	5.00	5.37	0.37	1.48_0	7.29_8
6.15	1.00_0	5.00	5.38	0.38	1.52_0	7.25_1
6.20	1.00_0	5.00	5.39	0.39	1.56_0	7.20_3

Table II B 2.4a

$\bar{n}_H$, $\bar{n}$, pL data for Cu(II) ethyl-2-propylacetoacetate system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.90	1.00_0	5.00	5.14	0.14	0.56_0	8.53_9
4.95	1.00_0	5.00	5.15	0.15	0.60_0	8.49_1
5.00	1.00_0	5.00	5.16	0.16	0.64_0	8.44_2
5.05	1.00_0	5.00	5.17	0.17	0.68_0	8.39_5
6.15	1.00_0	5.00	5.36	0.36	1.44_0	7.33_4
6.20	1.00_0	5.00	5.37	0.37	1.48_0	7.28_6
6.25	1.00_0	5.00	5.38	0.38	1.52_0	7.23_8
6.30	1.00_0	5.00	5.39	0.39	1.56_0	7.19_0

Table II B 2.5a

$\bar{n}_H$, $\bar{n}$, pL data for Cu(II) ethyl-2-isopropylacetoacetate system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.90	1.00_0	5.00	5.14	0.14	0.56_0	8.54_7
4.95	1.00_0	5.00	5.15	0.15	0.60_0	8.49_9
5.00	1.00_0	5.00	5.16	0.16	0.64_0	8.45_1
5.05	1.00_0	5.00	5.17	0.17	0.68_0	8.40_3
6.10	1.00_0	5.00	5.36	0.36	1.44_0	7.39_1
6.15	1.00_0	5.00	5.37	0.37	1.48_0	7.34_3
6.20	1.00_0	5.00	5.38	0.38	1.52_0	7.30_5
6.25	1.00_0	5.00	5.39	0.39	1.56_0	7.24_8

Table II B 2.6a

$\bar{n}_H$, $\bar{n}$, pL data for Cu(II) ethyl-2-butylacetoacetate system-30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.15	1.00_0	5.00	5.14	0.14	0.56_0	8.40_7
5.20	1.00_0	5.00	5.15	0.15	0.60_0	8.35_9
5.25	1.00_0	5.00	5.16	0.16	0.64_0	8.31_1
5.30	1.00_0	5.00	5.17	0.17	0.68_0	8.26_3
6.30	1.00_0	5.00	5.36	0.36	1.44_0	7.30_2
6.40	1.00_0	5.00	5.37	0.37	1.48_0	7.20_4
6.50	1.00_0	5.00	5.38	0.38	1.52_0	7.10_6
6.60	1.00_0	5.00	5.39	0.39	1.56_0	7.00_9

Table II B 3.1b

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

B	$\bar{n}_H$	V''	V'''	V'''-V''	$\bar{n}$	pL
5.90	1.00_0	5.00	5.08	0.08	0.32_0	7.25_6
5.95	1.00_0	5.00	5.09	0.09	0.36_0	7.20_8
6.00	1.00_0	5.00	5.10	0.10	0.40_0	7.16_1
6.05	1.00_0	5.00	5.11	0.11	0.44_0	7.11_2
6.10	1.00_0	5.00	5.12	0.12	0.48_0	7.06_4
6.15	1.00_0	5.00	5.13	0.13	0.52_0	7.01_6
6.95	1.00_0	5.01	5.32	0.31	1.24_0	6.25_6
7.00	1.00_0	5.01	5.34	0.33	1.32_0	6.20_6
7.05	1.00_0	5.01	5.36	0.35	1.40_0	6.16_1
7.10	1.00_0	5.02	5.38	0.36	1.44_0	6.10_2
7.15	1.00_0	5.02	5.39	0.37	1.48_0	6.06_4

Table II B 3.2b

$\bar{n}_H$, $\bar{n}$, pL data for Ni(II) ethyl-2-methylacetoacetate system - 30°C.

B	$\bar{n}_H$	V''	V'''	V'''-V''	$\bar{n}$	pL
6.25	1.00_0	5.00	5.08	0.08	0.32_0	7.05_9
6.30	1.00_0	5.00	5.09	0.09	0.36_0	7.01_2
6.35	1.00_0	5.00	5.10	0.10	0.40_0	6.96_4
6.40	1.00_0	5.00	5.11	0.11	0.44_0	6.91_5
6.45	1.00_0	5.00	5.12	0.12	0.48_0	6.86_7
6.50	1.00_0	5.00	5.13	0.13	0.52_0	6.81_9
7.15	1.00_0	5.01	5.34	0.33	1.32_0	6.20_9
7.20	1.00_0	5.02	5.36	0.34	1.36_0	6.16_1
7.25	1.00_0	5.02	5.37	0.35	1.40_0	6.11_3
7.30	1.00_0	5.02	5.39	0.37	1.48_0	6.06_5

Table II B 3.3b

$\bar{n}_H$, $\bar{n}$, pL data for Ni(II) ethyl-2-ethylacetoacetate system-30°C.

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	pL
6.40	1.00_0	5.00	5.08	0.08	0.32_0	6.94_1
6.45	1.00_0	5.00	5.09	0.09	0.36_0	6.89_3
6.50	1.00_0	5.00	5.10	0.10	0.40_0	6.84_4
6.55	1.00_0	5.00	5.11	0.11	0.44_0	6.79_6
6.60	1.00_0	5.00	5.12	0.12	0.48_0	6.74_8
6.65	1.00_0	5.00	5.13	0.13	0.52_0	6.70_0
7.35	1.00_0	5.03	5.35	0.32	1.28_0	6.03_8
7.40	1.00_0	5.03	5.37	0.34	1.36_0	5.99_2
7.45	1.00_0	5.03	5.39	0.36	1.44_0	5.94_7

Table II B 3.4b

$\bar{n}_H$, $\bar{n}$, pL data for Ni(II)ethyl-2-propylacetoacetate system-30°C.

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	pL
6.95	1.00_0	5.00	5.08	0.08	0.32_0	6.47_8
7.00	1.00_0	5.00	5.09	0.09	0.36_0	6.42_9
7.05	1.00_0	5.00	5.10	0.10	0.40_0	6.38_1
7.10	1.00_0	5.00	5.11	0.11	0.44_0	6.33_5
7.15	1.00_0	5.00	5.12	0.12	0.48_0	6.28_5
7.20	1.00_0	5.00	5.13	0.13	0.52_0	6.23_7
7.80	1.00_0	5.03	5.35	0.32	1.28_0	5.67_5
7.85	1.00_0	5.03	5.37	0.34	1.36_0	5.62_7
7.90	1.00_0	5.04	5.39	0.35	1.40_0	5.57_9
7.95	1.00_0	5.04	5.41	0.37	1.48_0	5.53_2
8.00	1.00_0	5.04	5.42	0.38	1.52_0	5.48_4

Table II B 3.5b

$\bar{n}_H$, $\bar{n}$, pL data for Ni(II) ethyl-2-isopropylacetoacetate system-30°C.

B	$\bar{n}_H$	V''	V'''	V'''-V''	$\bar{n}$	pL
6.90	1.00_0	5.00	5.08	0.08	0.32_0	6.53_5
6.95	1.00_0	5.00	5.09	0.09	0.36_0	6.48_7
7.00	1.00_0	5.00	5.10	0.10	0.40_0	6.43_9
7.05	1.00_0	5.00	5.11	0.11	0.44_0	6.39_1
7.10	1.00_0	5.00	5.12	0.12	0.48_0	6.34_3
7.15	1.00_0	5.00	5.13	0.13	0.52_0	6.29_5
7.70	1.00_0	5.03	5.34	0.31	1.24_0	5.77_3
7.75	1.00_0	5.03	5.35	0.32	1.28_0	5.72_5
7.80	1.00_0	5.03	5.37	0.34	1.36_0	5.68_5
7.85	1.00_0	5.04	5.40	0.36	1.44_0	5.63_7
7.90	1.00_0	5.04	5.42	0.38	1.52_0	5.58_9

Table II B 3.6b

$\bar{n}_H$, $\bar{n}$, pL data for Ni(II) ethyl-2-butylacetoacetate system-30°C.

B	$\bar{n}_H$	V''	V'''	V'''-V''	$\bar{n}$	pL
7.05	1.00_0	5.00	5.08	0.08	0.32_0	6.49_3
7.10	1.00_0	5.00	5.09	0.09	0.36_0	6.44_5
7.15	1.00_0	5.00	5.10	0.10	0.40_0	6.39_7
7.20	1.00_0	5.00	5.11	0.11	0.44_0	6.34_9
7.25	1.00_0	5.00	5.12	0.12	0.48_0	6.30_1
7.30	1.00_0	5.00	5.13	0.13	0.52_0	6.25_3
7.90	1.00_0	5.05	5.36	0.31	1.24_0	5.68_9
7.95	1.00_0	5.06	5.38	0.32	1.28_0	5.64_1
8.00	1.00_0	5.06	5.41	0.35	1.40_0	5.59_7
8.05	1.00_0	5.07	5.44	0.37	1.48_0	5.55_1
8.10	1.00_0	5.07	5.45	0.38	1.52_0	5.50_4

Table II B 4.1c

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
6.15	1.00_0	5.00	5.08	0.08	0.32_0	7.00_6
6.20	1.00_0	5.00	5.09	0.09	0.36_0	6.95_7
6.25	1.00_0	5.00	5.10	0.10	0.40_0	6.91_1
6.30	1.00_0	5.00	5.11	0.11	0.44_0	6.86_3
6.35	1.00_0	5.00	5.12	0.12	0.48_0	6.81_5
6.40	1.00_0	5.00	5.13	0.13	0.52_0	6.76_6
7.15	1.00_0	5.01	5.32	0.31	1.24_0	6.05_2
7.20	1.00_0	5.01	5.34	0.33	1.32_0	6.00_6
7.25	1.00_0	5.02	5.37	0.35	1.40_0	5.96_0
7.30	1.00_0	5.02	5.38	0.36	1.44_0	5.91_3
7.35	1.00_0	5.02	5.40	0.38	1.52_0	5.86_4

Table II B 4.2c

$\bar{n}_H$, $\bar{n}$, pL data for Zn(II) ethyl-2-methylacetoacetate system-30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
6.45	1.00_0	5.00	5.08	0.08	0.32_0	6.85_9
6.50	1.00_0	5.00	5.09	0.09	0.36_0	6.81_2
6.55	1.00_0	5.00	5.10	0.10	0.40_0	6.76_4
6.60	1.00_0	5.00	5.11	0.11	0.44_0	6.71_5
6.65	1.00_0	5.00	5.12	0.12	0.48_0	6.66_7
6.70	1.00_0	5.00	5.13	0.13	0.52_0	6.61_9
7.35	1.00_0	5.03	5.34	0.31	1.24_0	6.00_5
7.40	1.00_0	5.04	5.36	0.32	1.28_0	5.95_7
7.45	1.00_0	5.04	5.38	0.34	1.36_0	5.91_2
7.50	1.00_0	5.04	5.40	0.36	1.44_0	5.86_6
7.55	1.00_0	5.05	5.43	0.38	1.52_0	5.82_0

Table II B 4.3c

$\bar{n}_H$, $\bar{n}$, pL data for Zn(II) ethyl-2-ethylacetoacetate system-30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
6.70	1.00_0	5.00	5.08	0.08	0.32_0	6.64_1
6.75	1.00_0	5.00	5.09	0.09	0.36_0	6.59_3
6.80	1.00_0	5.00	5.10	0.10	0.40_0	6.54_5
6.85	1.00_0	5.00	5.11	0.11	0.44_0	6.49_7
6.90	1.00_0	5.00	5.12	0.12	0.48_0	6.44_9
6.95	1.00_0	5.00	5.13	0.13	0.52_0	6.40_1
7.60	1.00_0	5.04	5.35	0.31	1.24_0	5.78_6
7.65	1.00_0	5.05	5.38	0.33	1.32_0	5.74_1
7.70	1.00_0	5.05	5.40	0.35	1.40_0	5.69_5
7.75	1.00_0	5.05	5.42	0.37	1.48_0	5.64_9
7.80	1.00_0	5.06	5.45	0.39	1.56_0	5.60_3

Table II B 4.4c

$\bar{n}_H$, $\bar{n}$, pL data for Zn(II) ethyl-2-propylacetoacetate system-30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.05	1.00_0	5.00	5.08	0.08	0.32_0	6.38_6
7.10	1.00_0	5.00	5.09	0.09	0.36_0	6.33_8
7.15	1.00_0	5.00	5.10	0.10	0.40_0	6.28_9
7.20	1.00_0	5.00	5.11	0.11	0.44_0	6.24_1
7.25	1.00_0	5.00	5.12	0.12	0.48_0	6.19_3
7.30	1.00_0	5.00	5.13	0.13	0.52_0	6.14_5
7.95	1.00_0	5.04	5.35	0.31	1.24_0	5.53_1
8.00	1.00_0	5.05	5.38	0.33	1.32_0	5.48_5
8.05	1.00_0	5.05	5.40	0.35	1.40_0	5.43_9
8.10	1.00_0	5.05	5.42	0.37	1.48_0	5.39_4
8.15	1.00_0	5.05	5.44	0.39	1.56_0	5.34_8

Table II B 4.5c

$\bar{n}_H$, $\bar{n}$, pL data for Zn(II) ethyl-2-isopropylacetoacetate system-30°C.

B	$\bar{n}_H$	V"	V'''	V'''-V"	$\bar{n}$	pL
6.95	1.00_0	5.00	5.08	0.08	0.32_0	6.47_8
7.00	1.00_0	5.00	5.09	0.09	0.36_0	6.42_9
7.05	1.00_0	5.00	5.10	0.10	0.40_0	6.38_2
7.10	1.00_0	5.00	5.11	0.11	0.44_0	6.33_4
7.15	1.00_0	5.00	5.12	0.12	0.48_0	6.28_6
7.20	1.00_0	5.00	5.13	0.13	0.52_0	6.23_7
7.80	1.00_0	5.03	5.34	0.31	1.24_0	5.67_3
7.85	1.00_0	5.04	5.37	0.33	1.32_0	5.62_7
7.90	1.00_0	5.04	5.39	0.35	1.40_0	5.58_2
7.95	1.00_0	5.04	5.41	0.37	1.48_0	5.53_6
8.00	1.00_0	5.05	5.44	0.39	1.56_0	5.49_0

Table II B 4.6c

$\bar{n}_H$, $\bar{n}$, pL data for Zn(II) ethyl-2-butylacetoacetate system-30°C.

B	$\bar{n}_H$	V"	V'''	V'''-V"	$\bar{n}$	pL
7.25	1.00_0	5.00	5.08	0.08	0.32_0	6.29_4
7.30	1.00_0	5.00	5.09	0.09	0.36_0	6.24_6
7.35	1.00_0	5.01	5.11	0.10	0.40_0	6.19_8
7.40	1.00_0	5.01	5.12	0.11	0.44_0	6.13_9
7.50	1.00_0	5.02	5.14	0.12	0.48_0	6.05_2
7.55	1.00_0	5.02	5.15	0.13	0.52_0	6.00_3
8.15	1.00_0	5.07	5.38	0.31	1.24_0	6.43_9
8.20	1.00_0	5.07	5.39	0.32	1.28_0	5.39_2
8.25	1.00_0	5.08	5.42	0.34	1.36_0	5.34_6
8.30	1.00_0	5.09	5.44	0.35	1.40_0	5.29_8
8.35	1.00_0	5.09	5.45	0.36	1.44_0	5.25_0

Table II B 5.1d

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

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	pL
7.00	1.00_0	5.00	5.11	0.11	0.44_0	6.17_2
7.10	1.00_0	5.00	5.12	0.12	0.48_0	6.07_4
7.15	1.00_0	5.01	5.14	0.13	0.52_0	6.02_6
7.20	1.00_0	5.01	5.15	0.14	0.56_0	5.97_8
7.25	1.00_0	5.01	5.17	0.16	0.64_0	5.93_2

Table II B 5.2d

$\bar{n}_H$, $\bar{n}$, pL data for Be(II) ethyl-2-methylacetoacetate system-30°C.

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	pL
7.20	1.00_0	5.02	5.13	0.11	0.44_0	6.11_2
7.25	1.00_0	5.02	5.14	0.12	0.48_0	6.06_4
7.30	1.00_0	5.03	5.16	0.13	0.52_0	6.01_6
7.35	1.00_0	5.03	5.17	0.14	0.56_0	5.96_8
7.45	1.00_0	5.04	5.19	0.15	0.60_0	5.86_9

Table II B 5.3d

$\bar{n}_H$, $\bar{n}$, pL data for Be(II) ethyl-2-ethylacetoacetate system-30°C.

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	pL
7.45	1.00_0	5.03	5.14	0.11	0.44_0	5.90_2
7.50	1.00_0	5.04	5.16	0.12	0.48_0	5.85_4
7.55	1.00_0	5.04	5.17	0.13	0.52_0	5.80_6
7.65	1.00_0	5.05	5.19	0.14	0.56_0	5.70_8
7.70	1.00_0	5.05	5.20	0.15	0.60_0	5.66_0

Table II B 2.1a'

$\bar{n}$, pL, y, x, logβ_2, logK_1 and logK_2 data for Cu(II) ethylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^8	x x 10^{-8}	logβ_2	logK_1	log K_2
0.48	8.86	-6.6889	-0.4033	15.70	8.77	6.93
0.52	8.81	-6.9937	-0.4776	16.03	8.79	7.24
0.56	8.77	-7.4954	-0.5557	16.26	8.81	7.45
0.60	8.72	-7.8740	-0.6667	16.32	8.82	7.50
0.64	8.67	-8.3151	-0.8076	16.35	8.83	7.52
0.68	8.62	-8.8578	-0.9895	16.38	8.85	7.53
1.32	7.66	1.8852	4.6495	16.26	8.83	7.43
1.36	7.61	1.5388	4.3644	16.26	8.82	7.44
1.40	7.56	1.2708	4.1310	16.27	8.81	7.46
1.44	7.51	1.0591	3.9327	16.28	8.80	7.48
1.48	7.46	0.8893	3.7559	16.29	8.79	7.50

$\log \beta_2 = 16.22 + 0.08$
$\log K_1 = 8.81 \mp 0.01$
$\log K_2 = 7.41 \mp 0.07$

Table II B 2.2a'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) ethyl-2-methylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^8	x x 10^{-8}	log β_2	log K_1	log K_2
0.48	8.76	-5.3111	-0.5080	15.74	8.67	7.07
0.52	8.71	-5.5555	-0.6012	15.94	8.68	7.26
0.56	8.67	-5.9528	-0.6997	16.12	8.70	7.42
0.60	8.62	-5.9713	-0.8792	16.03	8.68	7.35
0.64	8.58	-6.7596	-0.9935	16.24	8.73	7.51
0.68	8.53	-7.2009	-1.2172	16.25	8.75	7.50
1.32	7.61	1.6802	5.2168	16.11	8.73	7.38
1.36	7.56	1.3717	4.8960	16.11	8.72	7.39
1.40	7.51	1.1326	4.6350	16.12	8.71	7.41
1.44	7.47	0.9659	4.3120	16.14	8.62	7.52
1.48	7.42	0.8109	4.1188	16.15	8.67	7.48

$\log \beta_2 = 16.08 + 0.06$
$\log K_1 = 8.69 \mp 0.03$
$\log K_2 = 7.39 \mp 0.08$

Table II B 2.3a'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) ethyl-2-ethylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^8	x x 10^{-8}	log β_2	log K_1	log K_2
0.56	8.55	-4.5164	-0.9222	15.81	8.57	7.24
0.60	8.50	-4.7438	-1.1067	15.87	8.58	7.29
0.64	8.46	-5.1277	-1.3097	15.97	8.60	7.37
0.68	8.41	-5.4627	-1.6046	15.98	8.61	7.37
1.44	7.35	0.7326	5.6852	15.91	8.61	7.30
1.48	7.30	0.6151	5.4394	15.92	8.60	7.32
1.52	7.25	0.5198	5.1904	15.93	8.59	7.34
1.56	7.20	0.4414	4.9578	15.94	8.57	7.37

log β_2 = 15.92 ± 0.03
log K_1 = 8.59 ± 0.01
log K_2 = 7.33 ± 0.03

Table II B 2.4a'

$\bar{n}$, pL, y, x, log β_2, log K_1, log K_2 data for Cu(II) ethyl-2-propylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^8	x x 10^{-8}	log β_2	log K_1	log K_2
0.56	8.54	-4.4130	-0.9438	15.81	8.56	7.25
0.60	8.49	-4.6353	-1.1326	15.87	8.57	7.30
0.64	8.44	-4.8961	-1.3717	15.90	8.58	7.32
0.68	8.40	-5.3378	-1.6421	15.97	8.61	7.36
1.44	7.33	0.6997	5.9525	15.88	8.61	7.27
1.48	7.29	0.6011	5.5564	15.90	8.58	7.32
1.52	7.24	0.5080	5.3113	15.85	8.57	7.28
1.56	7.19	0.4314	5.0733	15.92	8.56	7.36

log β_2 = 15.88 ± 0.05
log K_1 = 8.58 ± 0.01
log K_2 = 7.30 ± 0.04

Table II B 2.5a'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) ethyl-2-isopropylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^8	x x 10^{-8}	log β_2	log K_1	log K_2
0.56	8.55	-4.5164	-0.9222	15.92	8.56	7.36
0.60	8.50	-4.7438	-1.1067	15.96	8.57	7.39
0.64	8.45	-5.0106	-1.3403	15.98	8.58	7.40
0.68	8.40	-5.3378	-1.6421	15.99	8.58	7.41
1.44	7.39	0.8033	5.1850	15.94	8.60	7.34
1.48	7.34	0.6745	4.9519	15.95	8.59	7.36
1.52	7.31	0.5967	4.5212	15.98	8.55	7.43
1.56	7.25	0.4954	4.4180	15.98	8.55	7.43

log β_2 = 15.96 + 0.02
log K_1 = 8.57 ∓ 0.01
log K_2 = 7.39 ∓ 0.03

Table II B 2.6a'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Cu(II) ethyl-2-butylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^8	x x 10^{-8}	log β_2	log K_1	log K_2
0.56	8.41	-3.2717	-1.2730	15.61	8.43	7.18
0.60	8.36	-3.4364	-1.5277	15.65	8.44	7.21
0.64	8.31	-3.6295	-1.8503	15.68	8.44	7.24
0.68	8.26	-3.8671	-2.2666	15.69	8.45	7.24
1.44	7.30	0.6529	6.3789	15.73	8.35	7.38
1.48	7.20	0.4886	6.8358	15.68	8.42	7.26
1.52	7.11	0.3765	7.1649	15.64	8.46	7.18
1.56	7.01	0.2850	7.6780	15.60	8.50	7.10

log β_2 = 15.66 + 0.03
log K_1 = 8.44 ∓ 0.04
log K_2 = 7.22 ∓ 0.07

Table II B 3.1b'

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

$\bar{n}$	pL	$y \times 10^{6}$	$x \times 10^{-6}$	$\log \beta_2$	$\log K_1$	$\log K_2$
0.32	7.26	-8.5717	-0.1356	12.90	6.85	6.05
0.36	7.21	-9.1314	-0.1578	13.01	6.87	6.14
0.40	7.16	-9.6478	-0.1842	13.07	6.88	6.19
0.44	7.11	-10.1251	-0.2166	13.08	6.89	6.19
0.48	7.06	-10.5978	-0.2546	13.08	6.89	6.19
0.52	7.02	-11.3438	-0.2944	13.12	6.91	6.21
1.24	6.26	9.4024	1.7400	12.99	6.97	6.02
1.32	6.21	6.6899	1.3102	13.03	6.87	6.16
1.40	6.16	5.0592	1.0377	13.08	6.79	6.29
1.44	6.10	4.1202	1.0109	13.06	6.83	6.23
1.48	6.06	3.5399	0.9435	13.07	6.82	6.25

$\log \beta_2 = 13.04 \pm 0.04$
$\log K_1 = 6.87 \pm 0.03$
$\log K_2 = 6.17 \pm 0.07$

Table II B 3.2b'

$\bar{n}$, pL, y, x, $\log \beta_2$, $\log K_1$ and $\log K_2$ data for Ni(II) ethyl-2-methyl acetoacetate system - 30°C.

$\bar{n}$	pL	$y \times 10^{6}$	$x \times 10^{-6}$	$\log \beta_2$	$\log K_1$	$\log K_2$
0.32	7.06	-5.4028	-0.2151	12.88	6.57	6.31
0.36	7.01	-5.6419	-0.2554	12.86	6.57	6.29
0.40	6.96	-6.0827	-0.2922	12.90	6.58	6.32
0.44	6.92	-6.5367	-0.3348	12.92	6.59	6.33
0.48	6.87	-6.8426	-0.3943	12.89	6.58	6.31
0.52	6.82	-7.1554	-0.4668	12.86	6.55	6.31
1.32	6.21	6.6899	1.3102	12.90	6.52	6.38
1.36	6.16	5.4607	1.2298	12.88	6.59	6.29
1.40	6.11	4.5091	1.1643	12.85	6.64	6.21
1.48	6.07	3.6227	0.9220	12.90	6.53	6.37

$\log \beta_2 = 12.88 \pm 0.03$
$\log K_1 = 6.57 \pm 0.03$
$\log K_2 = 6.31 \pm 0.05$

Table II B 3.3b'

$\bar{n}$, pL, y, x, $\log \beta_2$, $\log K_1$ and $\log K_2$ data for Ni(II) ethyl-2-ethylacetoacetate system - 30°C.

$\bar{n}$	pL	$y \times 10^6$	$x \times 10^{-6}$	$\log \beta_2$	$\log K_1$	$\log K_2$
0.32	6.94	-4.0992	-0.2836	12.52	6.48	6.04
0.36	6.89	-4.3672	-0.3300	12.56	6.50	6.06
0.40	6.84	-4.6136	-0.3853	12.58	6.50	6.08
0.44	6.80	-4.9571	-0.4415	12.61	6.52	6.09
0.48	6.75	-5.1916	-0.5197	12.59	6.51	6.08
0.52	6.70	-5.4302	-0.6151	12.57	6.50	6.07
1.28	6.04	5.0125	2.3451	12.54	6.56	5.98
1.36	5.99	3.6928	1.8186	12.58	6.48	6.10
1.44	5.95	2.6825	1.4280	12.61	6.41	6.20

$\log \beta_2 = 12.57 + 0.03$
$\log K_1 = 6.49 \mp 0.03$
$\log K_2 = 6.08 \pm 0.03$

Table II B 3.4b'

$\bar{n}$, pL, y, x, $\log \beta_2$, $\log K_1$ and $\log K_2$ data for Ni(II) ethyl-2-propylacetoacetate system - 30°C.

$\bar{n}$	pL	$y \times 10^6$	$x \times 10^{-6}$	$\log \beta_2$	$\log K_1$	$\log K_2$
0.32	6.48	-1.4218	-0.8180	11.81	5.97	5.84
0.36	6.43	-1.5141	-0.9519	11.81	5.98	5.83
0.40	6.38	-1.5991	-1.1117	11.80	5.97	5.83
0.44	6.34	-1.7189	-1.2733	11.81	5.98	5.83
0.48	6.28	-1.7589	-1.5340	11.75	5.93	5.82
0.52	6.24	-1.8827	-1.7741	11.75	5.92	5.83
1.28	5.67	2.1380	5.4977	11.74	6.08	5.66
1.36	5.63	1.6116	4.1671	11.78	5.93	5.85
1.40	5.58	1.4830	3.5400	11.83	5.79	6.04
1.48	5.53	1.0448	3.1969	11.78	5.93	5.85
1.52	5.48	0.8828	3.0563	11.76	5.97	5.79

$\log \beta_2 = 11.78 + 0.02$
$\log K_1 = 5.94 \mp 0.06$
$\log K_2 = 5.83 \pm 0.06$

Table II B 3.5b'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Ni(II) ethyl-2-isopropylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log B_2	log K_1	log K_2
0.32	6.54	-1.6317	-0.7125	11.94	6.04	5.90
0.36	6.49	-1.7832	-0.8292	11.94	6.04	5.90
0.40	6.44	-1.8360	-0.9682	11.93	6.04	5.89
0.44	6.39	-1.9286	-1.1349	11.91	6.03	5.88
0.48	6.34	-2.0194	-1.3361	11.88	6.00	5.88
0.52	6.29	-2.1121	-1.5814	11.84	5.96	5.88
1.24	5.77	3.0427	5.3770	11.88	6.01	5.87
1.28	5.72	2.3997	4.8985	11.84	6.12	5.72
1.36	5.68	1.8084	3.7137	11.88	6.00	5.88
1.44	5.64	1.4285	2.9158	11.92	5.89	6.03
1.52	5.59	1.1373	2.3723	11.96	5.82	6.14

log β_2 = 11.90 + 0.03
log K_1 = 6.00 ∓ 0.05
log K_2 = 5.90 ∓ 0.06

Table II B 3.6b'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Ni(II) ethyl-2-butylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log β_2	log K_1	log K_2
0.32	6.49	-1.4542	-0.7994	11.79	6.00	5.79
0.36	6.44	-1.5491	-0.9304	11.80	6.01	5.79
0.40	6.40	-1.6746	-1.0616	11.82	6.03	5.79
0.44	6.35	-1.7589	-1.2443	11.80	6.02	5.78
0.48	6.30	-1.8417	-1.4650	11.78	6.01	5.77
0.52	6.25	-1.9266	-1.7337	11.74	5.98	5.76
1.24	5.69	2.5301	6.4663	11.73	6.05	5.68
1.28	5.64	1.9953	5.8911	11.70	6.12	5.58
1.40	5.60	1.3933	3.7680	11.80	5.86	5.94
1.48	5.55	1.0941	33.0528	11.83	5.78	6.05
1.52	5.50	0.9244	2.9187	11.81	5.86	5.95

log β_2 = 11.78 + 0.03
log K_1 = 5.97 ∓ 0.06
log K_2 = 5.81 ∓ 0.06

Table II B 4.1c'

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

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log β_2	log K_1	log K_2
0.32	6.92	-3.9150	-0.2969	12.59	6.44	6.15
0.36	6.87	-4.1697	-0.3456	12.61	6.45	6.16
0.40	6.82	-4.4033	-0.4037	12.61	6.45	6.15
0.44	6.77	-4.6272	-0.4730	12.59	6.45	6.14
0.48	6.72	-4.8455	-0.5568	12.57	6.43	6.14
0.52	6.68	-5.1858	-0.6441	12.57	6.43	6.14
1.32	6.06	4.7359	1.8508	12.61	6.38	6.23
1.36	6.01	3.8659	1.7372	12.58	6.45	6.13
1.40	5.96	3.1934	1.6440	12.56	6.49	6.07
1.48	5.91	2.5067	1.3325	12.60	6.42	6.18

log β_2 = 12.59 + 0.02
log K_1 = 6.44 $\mp$ 0.03
log K_2 = 6.15 $\mp$ 0.04

Table II B 4.2c'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Zn(II) ethyl-2-methylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log β_2	log K_1	log K_2
0.32	6.86	-3.4100	-0.3409	12.40	6.40	6.00
0.36	6.81	-3.6313	-0.3969	12.43	6.41	6.02
0.40	6.76	-3.8358	-0.4634	12.44	6.42	6.02
0.44	6.72	-4.1244	-0.5306	12.47	6.44	6.03
0.48	6.67	-4.3174	-0.6249	12.45	6.43	6.02
0.52	6.62	-4.5157	-0.7396	12.42	6.49	5.93
1.24	6.01	5.2872	3.0944	12.40	6.44	5.96
1.28	5.96	4.1710	2.8182	12.38	6.50	5.88
1.36	5.91	3.0713	2.1866	12.41	6.42	5.99
1.44	5.87	2.4260	1.7169	12.46	6.31	6.15
1.52	5.82	1.9306	1.3975	12.51	6.23	6.28

log β_2 = 12.43 + 0.03
log K_1 = 6.40 $\mp$ 0.04
log K_2 = 6.03 $\mp$ 0.06

Table II B 4.3c'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Zn(II) ethyl-2-ethylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log β_2	log K_1	log K_2
0.32	6.64	-2.0540	-0.5660	12.03	6.17	5.86
0.36	6.59	-2.1887	-0.6585	12.05	6.18	5.87
0.40	6.54	-2.3116	-0.7690	12.05	6.19	5.86
0.44	6.50	-2.4848	-0.8808	12.07	6.20	5.87
0.48	6.45	-2.6016	-1.0347	12.05	6.19	5.86
0.52	6.40	-2.7212	-1.2274	12.02	6.17	5.85
1.24	5.79	3.1853	5.1363	11.80	6.29	5.51
1.32	5.74	2.2664	3.8675	11.91	6.21	5.70
1.40	5.70	1.7543	2.9925	12.03	6.09	5.94
1.48	5.65	1.3771	2.4255	12.07	6.02	6.05
1.52	5.60	1.1636	1.9737	12.12	5.65	6.47

log β_2 = 12.01 + 0.05
log K_1 = 6.12 ∓ 0.07
log K_2 = 5.89 ∓ 0.09

Table II B 4.4c'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Zn(II) ethyl-2-propylacetoacetate system - 30°C.

$\bar{n}$	pL	y x 10^6	x x 10^{-6}	log β_2	log K_1	log K_2
0.32	6.39	-1.1551	-1.0065	11.53	5.93	5.60
0.36	6.34	-1.2305	-1.1713	11.55	5.94	5.61
0.40	6.29	-1.2997	-1.3677	11.55	5.94	5.61
0.44	6.24	-1.3655	-1.6029	11.54	5.94	5.60
0.48	6.19	-1.4295	-1.8874	11.52	5.93	5.59
0.52	6.15	-1.5303	-2.1826	11.52	5.93	5.59
1.24	5.53	1.7508	9.3448	11.44	6.05	5.39
1.32	5.49	1.2747	6.8765	11.48	5.92	5.56
1.40	5.44	0.9639	5.4465	11.51	5.85	5.66
1.48	5.39	0.7568	4.4135	11.55	5.78	5.77
1.56	5.35	0.6236	3.5278	11.61	5.66	5.95

log β_2 = 11.52 + 0.02
log K_1 = 5.90 ∓ 0.05
log K_2 = 5.63 ∓ 0.07

Table II B 4.5c'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Zn(II) ethyl-2-isopropylacetoacetate system - 30°C.

$\bar{n}$	pL	$y \times 10^6$	$x \times 10^{-6}$	log β_2	log K_1	log K_2
0.32	6.48	-1.4212	-0.8180	11.79	5.99	5.80
0.36	6.43	-1.5141	-0.9519	11.80	6.00	5.80
0.40	6.38	-1.5991	-1.1117	11.79	6.00	5.79
0.44	6.33	-1.6799	-1.3028	11.77	5.99	5.78
0.48	6.29	-1.7997	-1.4992	11.77	5.99	5.78
0.52	6.24	-1.8827	-1.7741	11.74	5.96	5.78
1.24	5.67	2.4165	6.7703	11.69	6.10	5.59
1.32	5.63	1.7598	4.9810	11.73	5.98	5.75
1.40	5.58	1.3307	3.9450	11.75	5.91	5.84
1.48	5.54	1.0691	3.1243	11.80	5.80	6.00
1.56	5.49	0.8608	2.5425	11.84	5.72	6.12

log β_2 = 11.77 $\pm$ 0.03
log K_1 = 5.95 $\pm$ 0.03
log K_2 = 5.82 $\pm$ 0.06

Table II B 4.6c'

$\bar{n}$, pL, y, x, log β_2, log K_1 and log K_2 data for Zn(II) ethyl-2-butylacetoacetate system - 30°C.

$\bar{n}$	pL	$y \times 10^6$	$x \times 10^{-6}$	log β_2	log K_1	log K_2
0.32	6.29	-0.9175	-1.2671	11.29	5.84	5.45
0.36	6.25	-1.0003	-1.4408	11.36	5.87	5.49
0.40	6.20	-1.0565	-1.6826	11.36	5.88	5.48
0.44	6.14	-1.0846	-2.0179	11.31	5.86	5.45
0.48	6.05	-1.0356	-2.6053	11.15	5.76	5.39
0.52	6.01	-1.1086	-3.0130	11.16	5.76	5.40
1.24	5.44	1.4229	11.4981	11.26	5.80	5.46
1.28	5.39	1.1220	10.4760	11.23	5.88	5.35
1.36	5.35	0.8457	7.9413	11.29	5.76	5.53
1.40	5.30	0.6983	7.5180	11.26	5.81	5.45
1.44	5.25	0.5820	7.1565	11.24	5.84	5.40

log β_2 = 11.26 $\pm$ 0.05
log K_1 = 5.82 $\pm$ 0.04
log K_2 = 5.44 $\pm$ 0.06

Table II B 5.1d'

$\bar{n}$, pL, $\log(1-\bar{n})/\bar{n}$ and pL-$\log(1-\bar{n})/\bar{n}$ data for Be(II) ethylacetoacetate system - 30°C.

$\bar{n}$	pL	$\log(1-\bar{n})/\bar{n}$	pL-$\log(1-\bar{n})/\bar{n}$
0.44_0	6.17_2	0.10_5	6.06_7
0.48_0	6.07_4	0.03_5	6.03_9
0.52_0	6.02_6	$\bar{1}.96_5$	6.06_1
0.56_0	5.97_8	$\bar{1}.89_5$	6.08_3
0.64_0	5.93_2	$\bar{1}.75_0$	6.18_2

$\log K_1 = 6.09 \pm 0.02$

Table II B 5.2d'

$\bar{n}$, pL, $\log(1-\bar{n})/\bar{n}$ and pL-$\log(1-\bar{n})/\bar{n}$ data for Be(II) ethyl-2-methylacetoacetate system - 30°C.

$\bar{n}$	pL	$\log(1-\bar{n})/\bar{n}$	pL-$\log(1-\bar{n})/\bar{n}$
0.44_0	6.11_2	0.10_5	6.00_7
0.48_0	6.06_4	0.03_5	6.02_9
0.52_0	6.01_6	$\bar{1}.96_5$	6.05_1
0.56_0	5.96_8	$\bar{1}.89_5$	6.07_3
0.60_0	5.86_9	$\bar{1}.82_4$	6.04_5

$\log K_1 = 6.04 \pm 0.02$

Table II B 5.3d'

$\bar{n}$, pL, $\log(1-\bar{n})/\bar{n}$ and pL-$\log(1-\bar{n})/\bar{n}$ data for Be(II) ethyl-2-ethylacetoacetate system - 30°C.

$\bar{n}$	pL	$\log(1-\bar{n})/\bar{n}$	pL-$\log(1-\bar{n})/\bar{n}$
0.44_0	5.79_7	0.10_5	5.69_2
0.48_0	5.81_9	0.03_5	5.78_4
0.52_0	5.84_0	$\bar{1}.96_5$	5.87_5
0.56_0	5.81_3	$\bar{1}.89_5$	5.91_8
0.60_0	5.83_6	$\bar{1}.82_4$	6.01_2

$\log K_1 = 5.85 \pm 0.04$

Fig.II B-10 : Be(II)ethylacetoacetate system - 30°C.

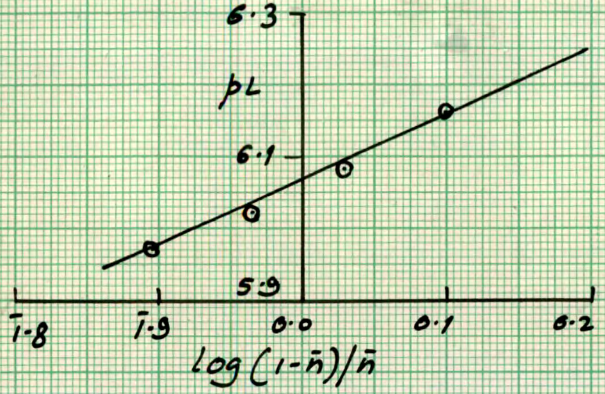


Fig.II B-11 : Be(II)ethyl-2-methyl-acetoacetate system -30°C.

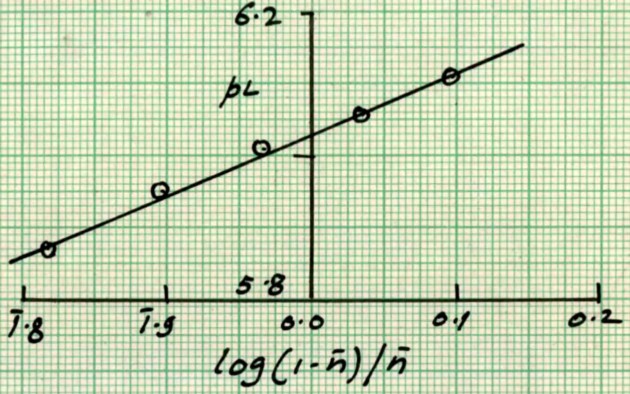


Fig.II B-12 : Be(II)ethyl-2-ethylacetoacetate system - 30°C.

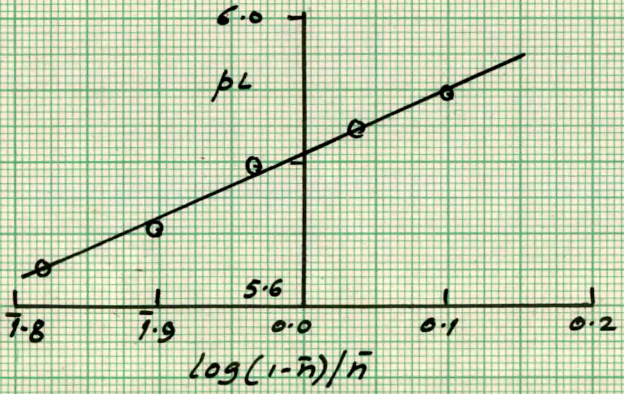


Table II B-6.0 : Proton and metal ligand stability constants of β-ketoesters - 30°C.

Ligand	$P_{K_1}^H$	Cu(II)		Ni(II)		Zn(II)		Be(II)	
		$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
Ethylacetoacetate	11.11	8.81±0.01,	7.41±0.07	6.87±0.03,	6.17±0.07	6.44±0.02,	6.15±0.04	6.09±0.02	-
Ethyl-2-methyl-acetoacetate	11.25	8.69±0.03,	7.39±0.08	6.57±0.03,	6.31±0.05	6.40±0.04,	6.03±0.06	6.04±0.02	-
Ethyl-2-ethyl-acetoacetate	11.29	8.59±0.01,	7.33±0.03	6.49±0.03,	6.08±0.01	6.12±0.07,	5.89±0.09	5.85±0.04	-
Ethyl-2-propyl-acetoacetate	11.37	8.58±0.01,	7.30±0.04	5.94±0.06,	5.83±0.06	5.90±0.05,	5.63±0.07	-	-
Ethyl-2-isopropyl-acetoacetate	11.38	8.57±0.01,	7.39±0.03	6.00±0.05,	5.90±0.06	5.95±0.03,	5.82±0.06	-	-
Ethyl-2-butyl-acetoacetate	11.49	8.44±0.04,	7.22±0.07	5.97±0.06,	5.81±0.06	5.82±0.04,	5.44±0.06	-	-

Section C

In case of β-diketone complexes there is coordination from two oxygen atoms. In order to see the effect of substituting one of the oxygen by nitrogen on the proton ligand and metal ligand formation constants, study of the complexes of Schiff bases obtained from acetylacetone and benzoylacetone was carried out. When monohydroxy alkylamines are condensed with β-diketones, they result in the formation of tridentate ligands. Study of the complexes of the tridentate Schiff bases in solution has invited the attention of a number of workers. Mehta and coworkers have determined the formation constants of a number of tridentate ligands obtained by the condensation of salicylaldehyde or 2-hydroxy-1-naphthaldehyde with β-alanine, anthranilic acid[22-27] or acetylacetone or benzoylacetone with β-alanine, anthranilic acid.[28-32]

In the present study, Irving-Rossotti titration technique[11] has been applied to determine the formation constants of complexes of Cu(II) and Ni(II) with tridentate Schiff bases formed by the condensation of acetylacetone and benzoylacetone with monohydroxy alkylamines. The tridentate ligands used are as follows : 4-(2-hydroxyethylimino)pentane-2-one (HEA) or 4-(2-hydroxyethylimino)-4-phenylbutane-2-one (HEBA) or 4-(2-hydroxypropylimino)pentane-2-one(HPA) or 4-(2-hydroxypropylimino)-4-phenylbutane-2-one(HPBA).

Experimental :

Preparation of ligands (Schiff bases) :

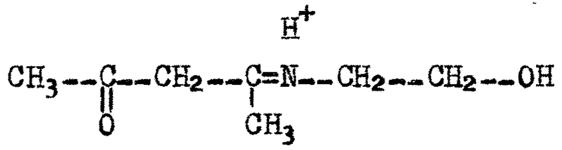
The Schiff base was prepared[33] by refluxing a mixture of diketone and ethanolamine or iso-propanolamine in molar ratio on a water bath for half an hour in an apparatus provided with a water separator. After the reflux the contents of the flask were cooled, when brownish yellow coloured solid mass separated out. It was recrystallised from methanol, analysed and preserved in a vacuum desiccator.

Other chemicals used were same as in section A of this chapter. The instruments used and the titrations carried out are similar to section A Chapter II. Titrations were carried out in 50% dioxan medium and the pH corrections were made as before. Tables and figures are given in III C 1.1 to III C 1.4 and III C 1 to III C 4, respectively.

Schiff bases are known to be susceptible to hydrolysis. The titrations were, therefore, carried out using four different concentrations of the ligand - 0.1M, 0.05M, 0.02M, and 0.01M solutions. In case of 0.02M and 0.01M solutions, the values of proton ligand and metal ligand formation constants of the Schiff base almost correspond to those of original β-diketone. This shows that the Schiff base gets hydrolysed. For 0.05M and 0.1M concentration the values are higher and are constant. This shows that at concentrations higher than 0.05M, hydrolysis does not take place.

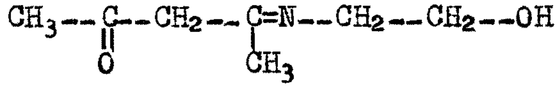
Determination of proton ligand and metal ligand formation constants :

As seen in Irving-Rossotti titration curves (fig.III C 1 to III C 4) at low pH the ligand titration curves, 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 -



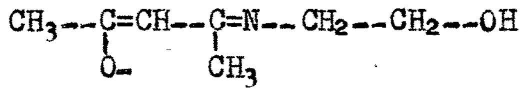
$CH_3{-}\underset{\overset{\|}{O}}{C}{-}CH_2{-}\underset{\overset{|}{CH_3}}{C}{=}\overset{H^+}{N}{-}CH_2{-}CH_2{-}OH$

As the pH increases the ligand curve tries to merge with the acid curve due to formation of



$CH_3{-}\underset{\overset{\|}{O}}{C}{-}CH_2{-}\underset{\overset{|}{CH_3}}{C}{=}N{-}CH_2{-}CH_2{-}OH$

A stage comes when the ligand curve crosses the acid curve. At this pH the ligand gives out the enolic H^+.



$CH_3{-}\underset{\overset{|}{O^-}}{C}{=}CH{-}\underset{\overset{|}{CH_3}}{C}{=}N{-}CH_2{-}CH_2{-}OH$

Thus the present ligands are characterised by two P_K^H values. The $P_{K_1}^H$ is due to the association of the enolic proton. The basic nitrogen absorbs hydrogen from the solution and gets protonated. The association of this proton corresponds to $P_{K_2}^H$. The -OH of the alkylamine part of the Schiff base is weakly dissociating and remains undissociated till pH 9.

The equations used for the determination of $\bar{n}_H$, $\bar{n}$ and pL are same as in section A of this chapter. The average value of proton ligand and metal ligand formation constants have been computed by linear plot method as in section A of this chapter.

The basicity of the ligands are in the following order - HEA $<$ HEBA $<$ HPA $<$ HPBA.

It has been observed earlier that the $P_{K_1}^H$ of benzoylacetone is more than that of acetylacetone. Due to the greater enol content in benzoylacetone the hydrogen bonding is more.

Thus the number of available protons is less for titration as compared to acetylacetone and hence the basicity of benzoylacetone is more than that of acetylacetone. Increase in the value of K_1^H in HEBA and HPBA can also be explained on the same lines.

$^PK_2^H$ in the Schiff base corresponds to the association of the H^+ with the basic azomethine nitrogen atom. It is observed that $^PK_2^H$ values of HEBA and HPBA are more than that of HEA and HPA.

In the binary complexes of the present ligands it is observed that the formation constants are significantly higher than the original β-diketones. It has been shown earlier[34] that the β-ketoimine form more stable complexes than the β-diketone. This is because of the strongly basic C=N nitrogen. In the present ligands, in addition to the strongly basic nitrogen, there is also possibility of coordination from the -OH of the ethanolamine part, thus forming a stable tridentate chelate. The increase in stability of Schiff base complexes may be due to the more basic nitrogen or because of the tridentate nature of the ligand. The bidentate or tridentate nature has been further confirmed in the ternary complexes, reported in the next chapter.

Table IIC 1.1

N = 0.2M V° = 50 ml. T°_L = 0.01M T°_M = 0.001M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		HEA		Cu(II)		Ni(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	1.85	0.00	2.05	0.00	2.05	0.00	2.05
1.00	1.90	0.50	2.15	0.50	2.15	0.50	2.15
2.00	2.00	1.00	2.25	1.00	2.20	1.00	2.20
3.00	2.20	1.50	2.50	1.50	2.50	1.50	2.50
4.00	2.40	2.00	2.80	2.00	2.80	2.00	2.80
4.50	2.75	2.10	2.90	2.10	2.90	2.20	3.05
4.60	2.85	2.20	3.05	2.20	3.05	2.40	3.75
4.70	3.00	2.30	3.30	2.30	3.10	2.50	4.25
4.80	3.25	2.35	3.45	2.40	3.15	2.60	4.85
4.85	3.35	2.40	4.05	2.50	3.25	2.70	5.45
4.90	3.65	2.43	6.00	2.60	3.35	2.80	6.00
4.93	4.00	2.47	6.90	2.70	3.55	2.90	6.60
4.96	4.75	2.50	7.25	2.80	4.25	3.00	7.25
4.98	5.25	2.60	7.75	2.90	5.40	3.10	7.65
5.00	7.85	2.70	8.00	3.00	6.35	3.20	7.90
5.02	8.60	2.80	8.20	3.10	7.30	3.40	8.25
5.05	9.20	2.90	8.35	3.20	7.90	3.60	8.55
5.08	9.75	3.00	8.45	3.30	8.35	3.80	8.80
5.10	10.00	3.50	8.70	3.40	8.60	4.00	8.90
5.15	10.50	4.00	8.90	3.50	8.70	4.30	9.05
		4.50	9.20	3.60	8.75	4.60	9.25
		5.00	9.50				
		5.50	9.65				
		6.00	9.85				

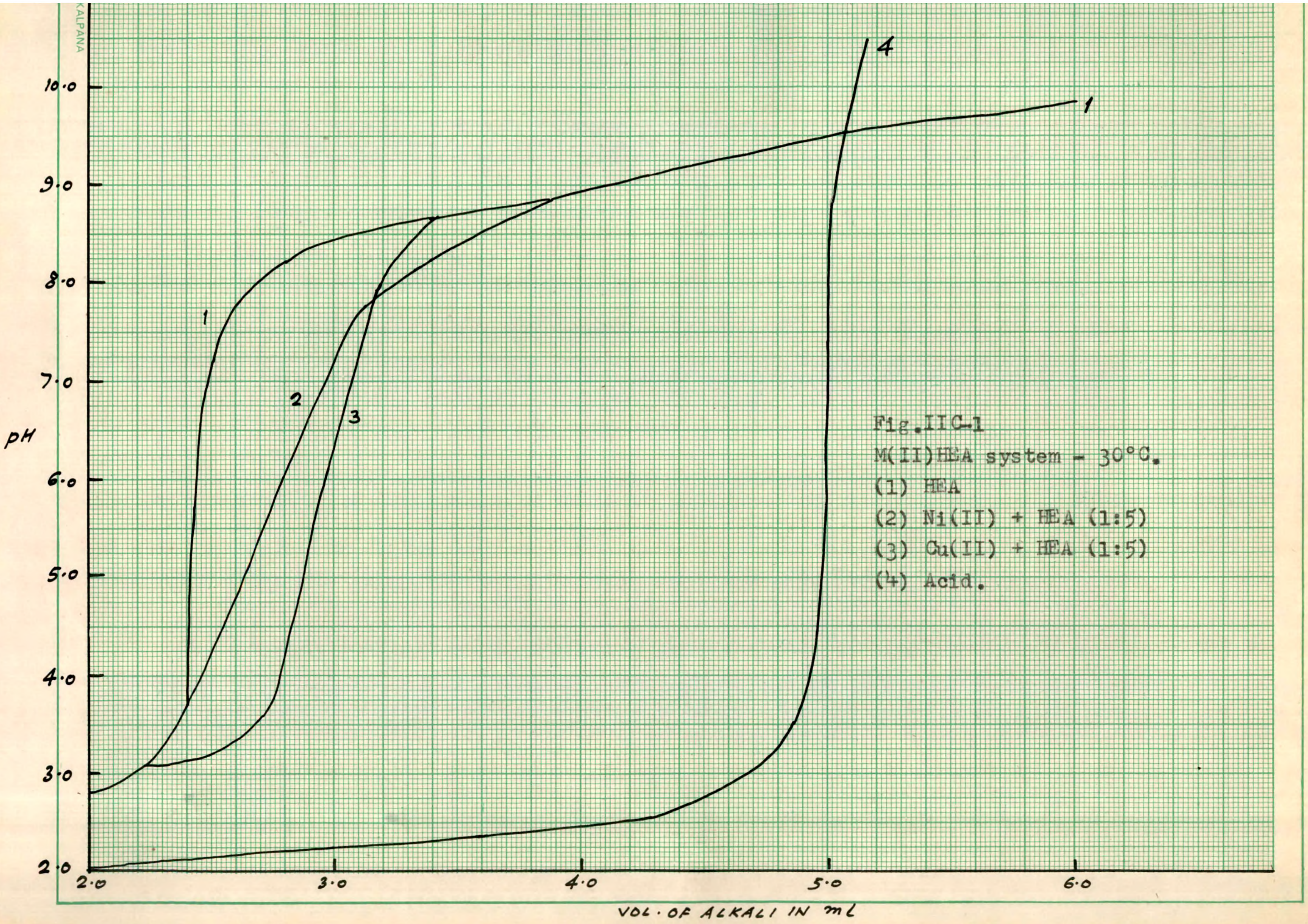


Fig. IIC-1
M(II)HEA system - 30°C.
(1) HEA
(2) Ni(II) + HEA (1:5)
(3) Cu(II) + HEA (1:5)
(4) Acid.

Table IIC 1.2

$N = 0.2M$ $V^\circ = 50$ ml. $T^\circ_L = 0.01M$ $T^\circ_M = 0.001M$

$E^\circ = 0.02M$ $\mu = 0.2M$ $t = 30^\circ C.$

Perchloric acid		HEBA		Cu(II)		Ni(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	1.85	0.00	2.05	0.00	2.05	0.00	2.05
1.00	1.90	0.50	2.15	0.50	2.15	0.50	2.15
2.00	2.00	1.00	2.25	1.00	2.25	1.00	2.25
3.00	2.20	1.50	2.50	1.50	2.50	1.50	2.50
4.00	2.40	2.00	2.85	2.00	2.85	2.00	2.85
4.50	2.75	2.10	2.95	2.10	2.95	2.20	3.10
4.60	2.85	2.20	3.10	2.20	3.10	2.40	3.80
4.70	3.00	2.30	3.35	2.30	3.15	2.50	4.40
4.80	3.25	2.35	3.55	2.40	3.20	2.60	4.95
4.85	3.35	2.40	3.80	2.50	3.25	2.70	5.50
4.90	3.65	2.43	5.25	2.60	3.45	2.80	6.00
4.93	4.00	2.45	6.60	2.70	3.65	2.90	6.60
4.96	4.75	2.50	7.45	2.80	3.95	3.00	7.20
4.98	5.25	2.60	7.85	2.90	4.35	3.20	7.90
5.00	7.85	2.70	8.05	3.00	5.75	3.40	8.25
5.02	8.60	2.80	8.25	3.10	8.00	3.60	8.50
5.05	9.20	2.90	8.40	3.20	8.45	3.80	8.70
5.08	9.75	3.00	8.50	3.30	8.70	4.00	8.85
5.10	10.00	3.50	8.80	3.40	8.75	4.30	9.05
		4.00	9.05	3.50	8.80	4.60	9.30
		4.50	9.20	3.60	8.90		
		5.00	9.45				
		5.50	9.80				
		6.00	10.15				

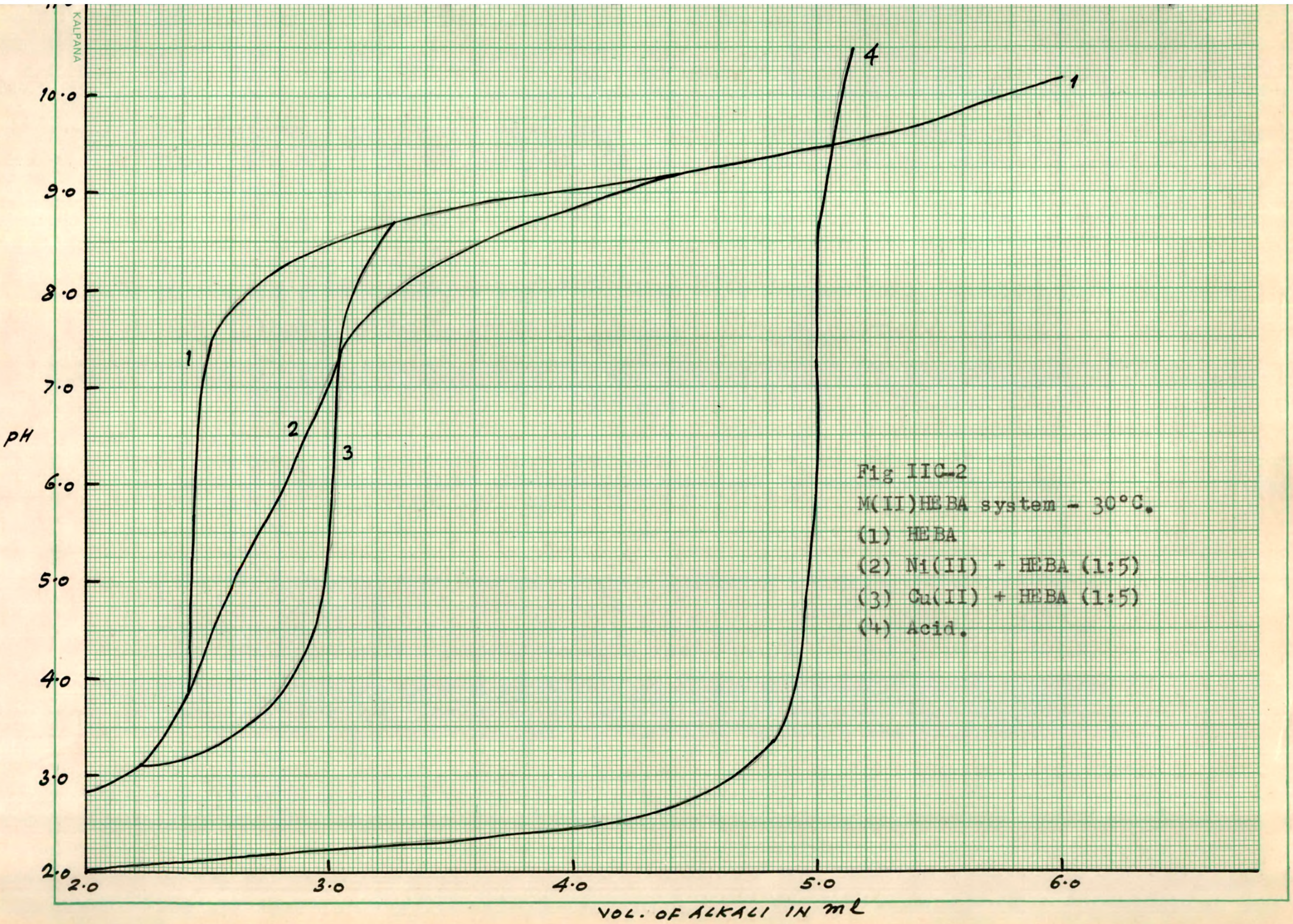


Fig IIC-2

M(II)HEBA system - 30°C.

(1) HEBA

(2) Ni(II) + HEBA (1:5)

(3) Cu(II) + HEBA (1:5)

(4) Acid.

Table IIc 1.3

N = 0.2M V° = 50 ml. T°_L = 0.01M T°_M = 0.001M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		HPA		Cu(II)		Ni(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	1.85	0.00	2.05	0.00	2.05	0.00	2.05
1.00	1.90	0.50	2.15	0.50	2.15	0.50	2.15
2.00	2.00	1.00	2.25	1.00	2.25	1.00	2.25
3.00	2.20	1.50	2.50	1.50	2.50	1.50	2.50
4.00	2.40	2.00	2.80	2.00	2.80	2.00	2.80
4.50	2.75	2.10	2.95	2.10	2.95	2.20	3.10
4.60	2.85	2.20	3.10	2.20	3.10	2.40	3.90
4.70	3.00	2.30	3.40	2.30	3.15	2.50	4.45
4.80	3.25	2.35	3.60	2.40	3.15	2.60	4.90
4.85	3.35	2.40	3.90	2.50	3.20	2.70	5.40
4.90	3.65	2.42	5.75	2.60	3.35	2.80	5.95
4.93	4.00	2.44	6.45	2.70	3.65	2.90	6.50
4.96	4.75	2.46	6.85	2.80	4.10	3.00	7.00
4.98	5.25	2.48	7.25	2.90	4.75	3.10	7.45
5.00	7.85	2.50	7.50	3.00	6.50	3.20	7.75
5.02	8.60	2.60	7.95	3.10	8.00	3.40	8.15
5.05	9.20	2.70	8.15	3.20	8.50	3.60	8.40
5.08	9.75	2.80	8.30	3.30	8.75	3.80	8.60
5.10	10.00	3.00	8.55	3.40	8.80	4.00	8.85
5.15	10.50	3.50	8.85	3.50	8.85	4.30	9.15
		4.00	9.05	3.60	8.90	4.60	9.40
		4.50	9.35				
		5.00	9.60				
		5.50	9.90				
		6.00	10.20				

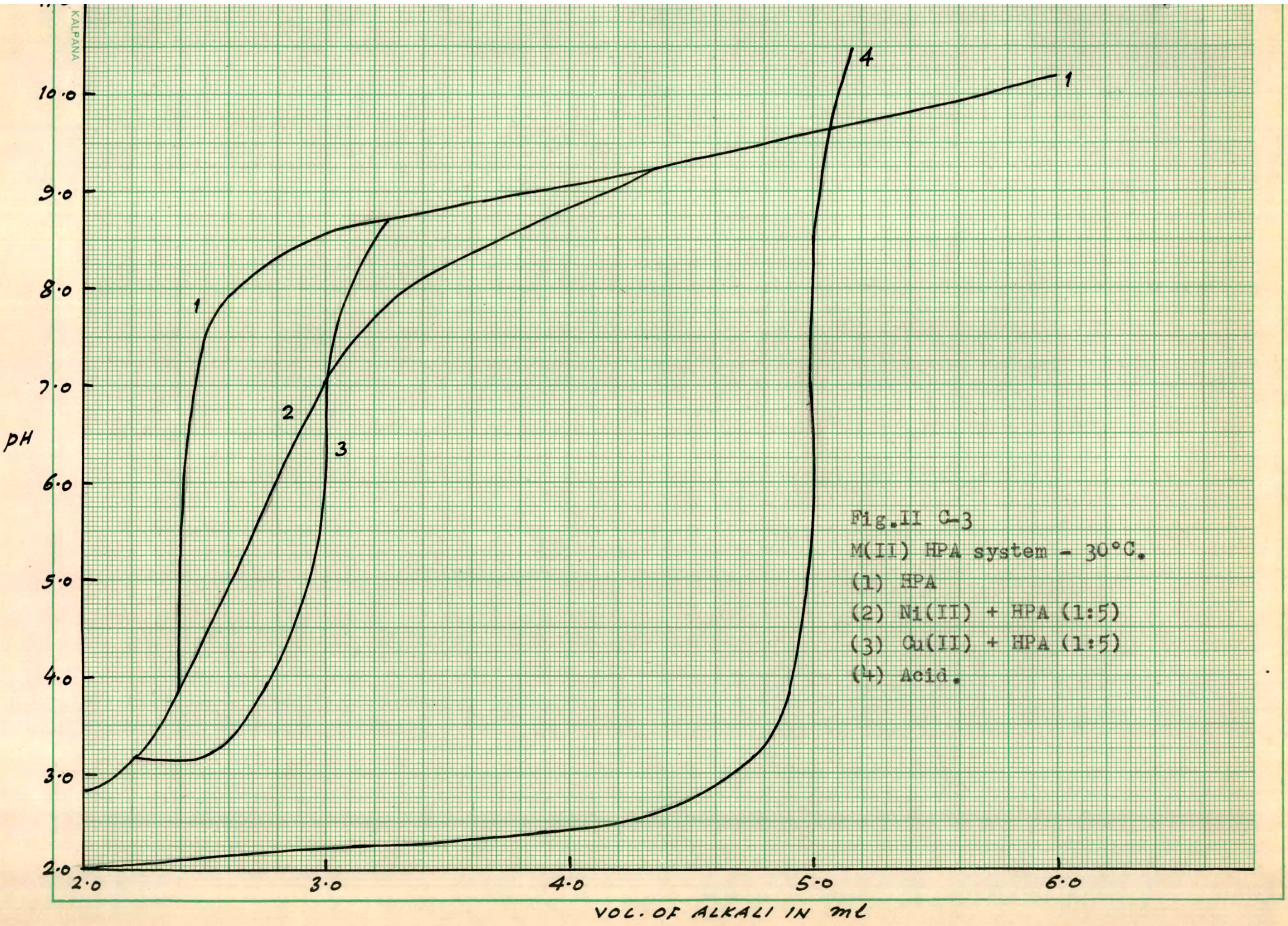


Fig.II C-3
M(II) HPA system - 30°C.
(1) HPA
(2) Ni(II) + HPA (1:5)
(3) Cu(II) + HPA (1:5)
(4) Acid.

Table IIC 1.4

N = 0.2M V° = 50 ml. T°_{L} = 0.01M T°_{M} = 0.001M

E° = 0.02M μ = 0.2M t = 30°C.

Perchloric acid		HPBA		Cu(II)		Ni(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	1.85	0.00	2.05	0.00	2.05	0.00	2.05
1.00	1.90	0.50	2.15	0.50	2.15	0.50	2.15
2.00	2.00	1.00	2.25	1.00	2.25	1.00	2.25
3.00	2.20	1.50	2.50	1.50	2.50	1.50	2.50
4.00	2.40	2.00	2.85	2.00	2.85	2.00	2.85
4.50	2.75	2.10	2.95	2.10	2.95	2.20	3.15
4.60	2.85	2.20	3.15	2.20	3.05	2.40	3.90
4.70	3.00	2.30	3.40	2.30	3.10	2.50	4.30
4.80	3.25	2.35	3.65	2.40	3.15	2.60	4.75
4.85	3.35	2.40	4.00	2.50	3.25	2.70	5.20
4.90	3.65	2.43	5.45	2.60	3.45	2.80	5.70
4.93	4.00	2.46	6.50	2.70	3.70	2.90	6.40
4.96	4.75	2.48	7.00	2.80	4.00	3.00	7.00
4.98	5.25	2.50	7.50	2.90	4.50	3.20	7.75
5.00	7.85	2.60	7.95	3.00	6.25	3.40	8.15
5.02	8.60	2.70	8.25	3.10	7.60	3.60	8.50
5.05	9.20	2.80	8.40	3.20	8.05	3.80	8.70
5.08	9.75	2.90	8.55	3.30	8.40	4.00	8.90
5.10	10.00	3.00	8.65	3.40	8.70	4.30	9.25
5.15	10.50	3.50	8.95	3.50	8.95	4.60	9.45
		4.00	9.15	3.60	9.00		
		4.50	9.40				
		5.00	9.65				
		5.50	9.95				
		6.00	10.50				

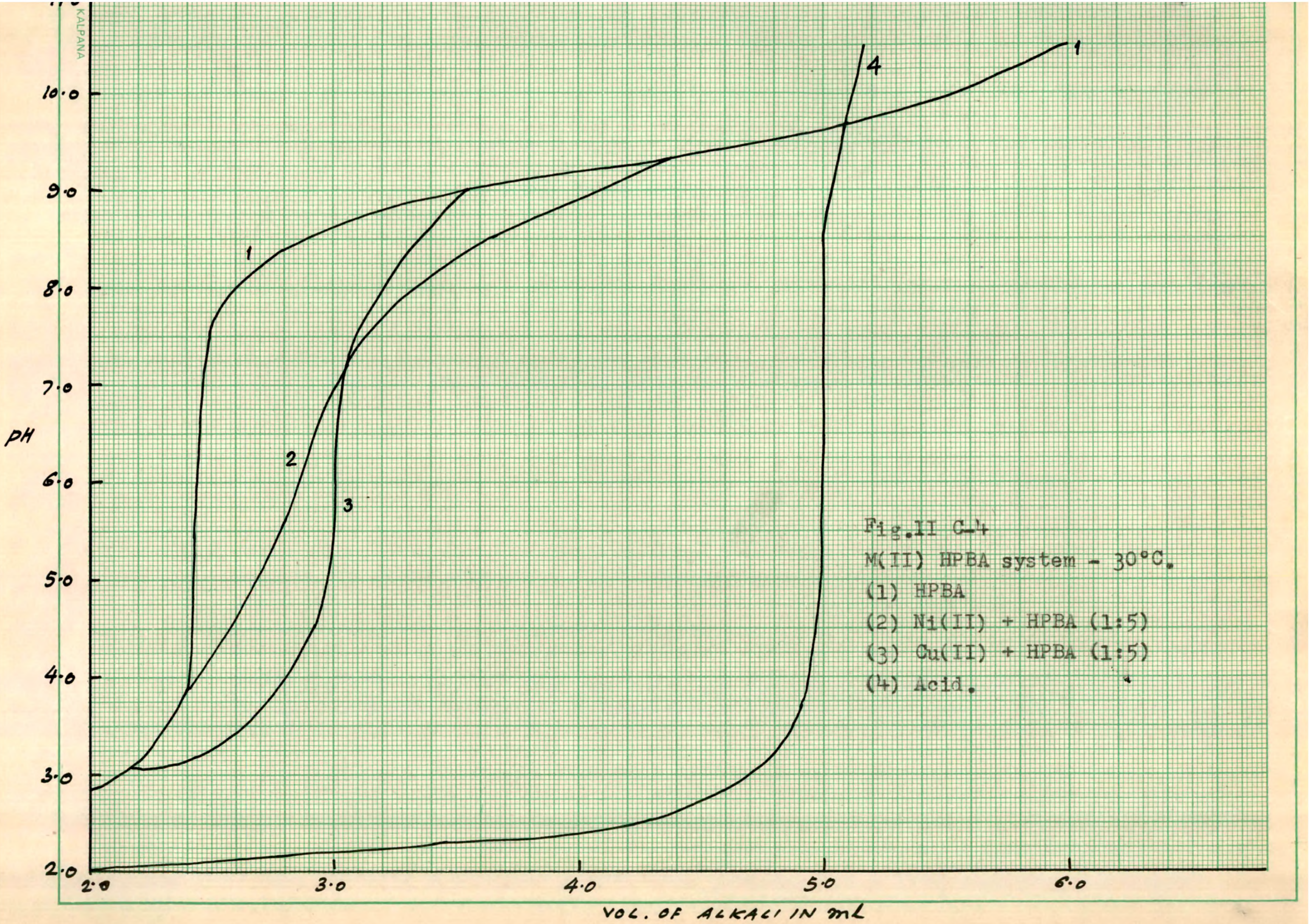


Fig.II C-4
M(II) HPBA system - 30°C.
(1) HPBA
(2) Ni(II) + HPBA (1:5)
(3) Cu(II) + HPBA (1:5)
(4) Acid.

Table II C 2.1a

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data for Cu(II) HEA system-30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
3.30	2.00_0	2.30	2.54	0.24	0.48_2	0.03_1	14.32_3	14.29_2
3.35	2.00_0	2.32	2.59	0.27	0.54_2	$\bar{1}.92_7$	14.22_6	14.29_9
3.40	2.00_0	2.34	2.62	0.28	0.56_2	$\bar{1}.89_0$	14.12_7	14.23_7
3.45	2.00_0	2.35	2.65	0.30	0.60_2	$\bar{1}.81_8$	14.02_7	14.20_9

$\log K_1 = 14.26 \pm 0.02$

Table II C 2.2a

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data for Cu(II) HEBA system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
3.35	2.00_0	2.30	2.54	0.24	0.48_2	0.03_1	14.68_3	14.65_2
3.40	2.00_0	2.32	2.58	0.26	0.52_2	$\bar{1}.96_2$	14.58_5	14.62_3
3.45	2.00_0	2.33	2.60	0.27	0.54_2	$\bar{1}.92_7$	14.48_6	14.55_9
3.50	2.00_0	2.34	2.64	0.30	0.60_2	$\bar{1}.81_8$	14.38_9	14.57_1
3.55	2.00_0	2.36	2.67	0.31	0.62_2	$\bar{1}.78_4$	14.29_0	14.50_6

$\log K_1 = 14.59 \pm 0.05$

Table II C 2.3a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL$-\log(1-\bar{n})/\bar{n}$ data for Cu(II) HPA system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL$-\log(1-\bar{n})/\bar{n}$
3.20	2.00_0	2.24	2.48	0.24	0.48_2	0.03_1	15.06_2	15.03_1
3.25	2.00_0	2.26	2.54	0.28	0.56_2	$\bar{1}.89_0$	14.96_7	15.07_7
3.30	2.00_0	2.28	2.58	0.30	0.60_3	$\bar{1}.81_8$	14.86_0	15.05_1
3.35	2.00_0	2.29	2.62	0.32	0.64_3	$\bar{1}.74_5$	14.77_1	15.02_6
3.40	2.00_0	2.30	2.63	0.33	0.66_3	$\bar{1}.70_6$	14.67_2	14.96_6

$\log K_1 = 15.03 \pm 0.03$

Table II C 2.4a

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL$-\log(1-\bar{n})/\bar{n}$ data for Cu(II) HPBA system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL$-\log(1-\bar{n})/\bar{n}$
3.25	2.00_0	2.25	2.49	0.24	0.48_2	0.03_1	15.27_2	15.24_1
3.30	2.00_0	2.27	2.52	0.25	0.50_2	$\bar{1}.99_7$	15.17_4	15.17_2
3.35	2.00_0	2.29	2.55	0.26	0.52_2	$\bar{1}.96_2$	15.07_5	15.11_3
3.40	2.00_0	2.30	2.57	0.27	0.54_2	$\bar{1}.92_7$	14.97_6	15.04_9
3.45	2.00_0	2.32	2.60	0.28	0.56_1	$\bar{1}.89_3$	14.87_7	14.98_4

$\log K_1 = 15.11 \pm 0.05$

Fig.II C-5 : Cu(II)HEA system - 30°C.

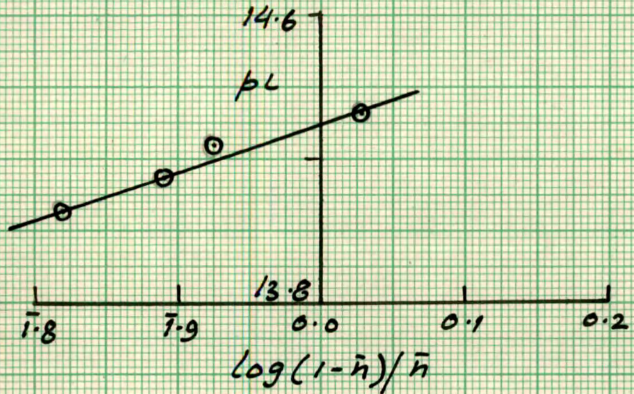


Fig.II C-6 : Cu(II)HEBA system - 30°C.

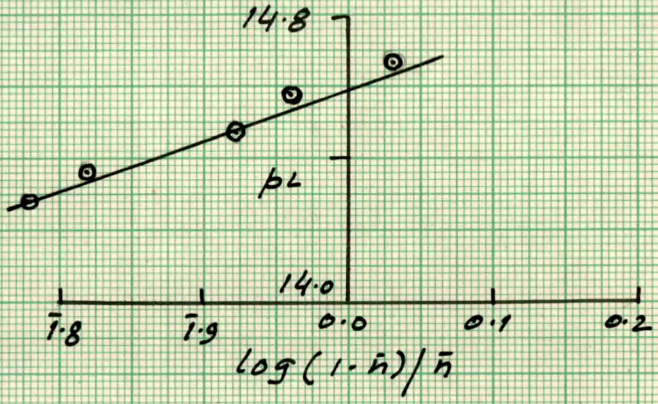


Fig.II C-7 : Cu(II)HPA system - 30°C.

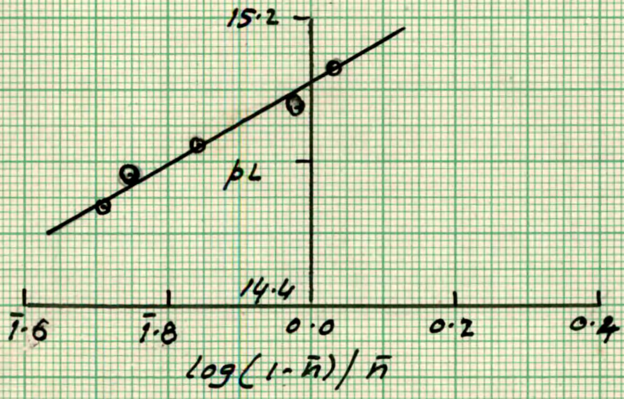


Fig.II C-8 : Cu(II)HPBA system - 30°C.

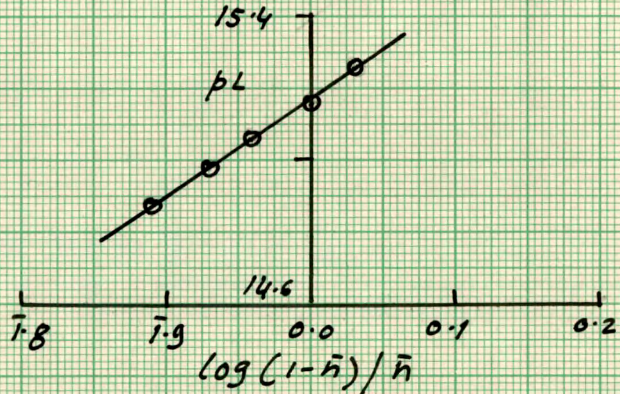


Table II C 2.5b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni(II) HEA system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.20	2.00_0	2.42	2.66	0.24	0.48_1	0.03_1	10.52_4	10.49_3
5.25	2.00_0	2.42	2.67	0.25	0.50_1	$\bar{1}.99_8$	10.42_5	10.42_7
5.30	2.00_0	2.42	2.68	0.26	0.52_1	$\bar{1}.96_4$	10.32_6	10.36_2
5.40	2.00_0	2.42	2.70	0.28	0.56_2	$\bar{1}.89_3$	10.12_8	10.23_5
5.45	2.00_0	2.42	2.71	0.29	0.58_1	$\bar{1}.85_6$	10.02_9	10.17_3

$\log K_1 = 10.34 \pm 0.06$

Table II C 2.6b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni(II) HEBA system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.35	2.00_0	2.44	2.67	0.23	0.46_0	0.06_9	10.58_3	10.51_4
5.40	2.00_0	2.44	2.68	0.24	0.48_0	0.03_5	10.48_4	10.44_9
5.45	2.00_0	2.44	2.69	0.25	0.50_0	-	10.38_5	10.38_5
5.50	2.00_0	2.44	2.70	0.26	0.52_0	$\bar{1}.96_5$	10.28_6	10.32_1
5.55	2.00_0	2.44	2.71	0.27	0.54_1	$\bar{1}.92_9$	10.18_7	10.25_8

$\log K_1 = 10.39 \pm 0.05$

Table II C 2.7b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni(II) HPA system - 30°C.

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.10	2.00_0	2.40	2.64	0.24	0.48_1	0.03_3	11.26_4	11.23_1
5.15	2.00_0	2.40	2.65	0.25	0.50_1	$\bar{1}.99_8$	11.16_5	11.16_7
5.20	2.00_0	2.40	2.66	0.26	0.52_1	$\bar{1}.96_4$	11.06_5	11.10_1
5.25	2.00_0	2.41	2.68	0.27	0.54_1	$\bar{1}.92_0$	10.96_6	11.03_7
5.35	2.00_0	2.41	2.69	0.28	0.56_1	$\bar{1}.89_3$	10.76_8	10.87_5

$\log K_1 = 11.08 \pm 0.07$

Table II C 2.8b

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data for Ni(II) HPBA system - 30°C.

B	$\bar{n}_H$	V''	V'''	$V'''-V''$	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.05	2.00_0	2.42	2.67	0.25	0.50_0	-	11.67_5	11.67_5
5.10	2.00_0	2.42	2.68	0.26	0.52_0	$\bar{1}.96_5$	11.57_6	11.61_1
5.15	2.00_0	2.42	2.69	0.27	0.54_1	$\bar{1}.92_9$	11.47_7	11.54_8
5.20	2.00_0	2.42	2.70	0.28	0.56_1	$\bar{1}.89_3$	11.37_7	11.48_4
5.25	2.00_0	2.43	2.72	0.29	0.58_1	$\bar{1}.85_6$	11.27_9	11.42_3

$\log K_1 = 11.55 \pm 0.05$

Fig.II C-9 : Ni(II)HEA system - 30°C.

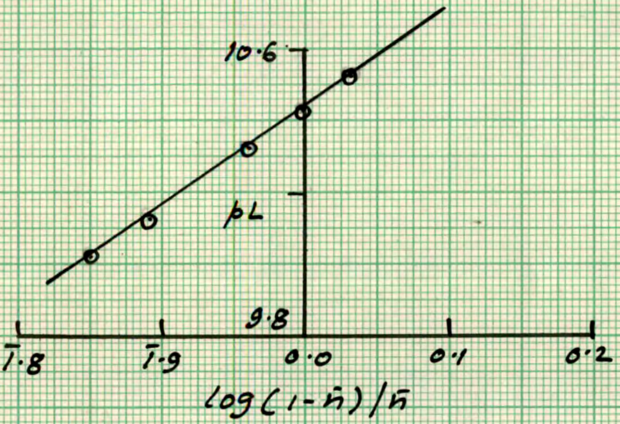


Fig.II C-10 : Ni(II)HEBA system - 30°C.

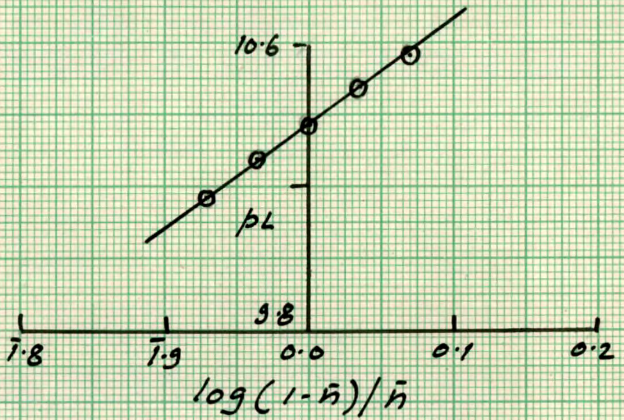


Fig.II C-11 : Ni(II)HPA system - 30°C.

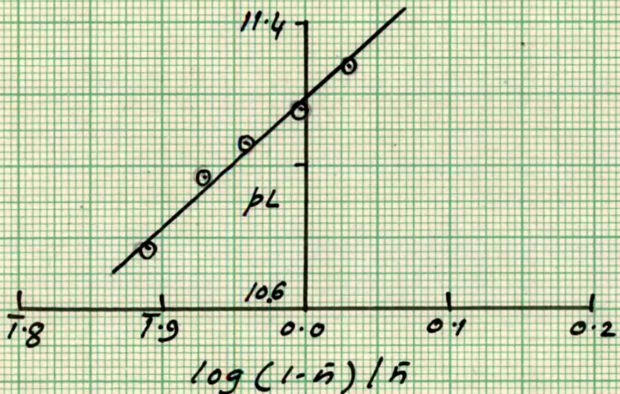


Fig.II C-12 : Ni(II)HPBA system - 30°C.

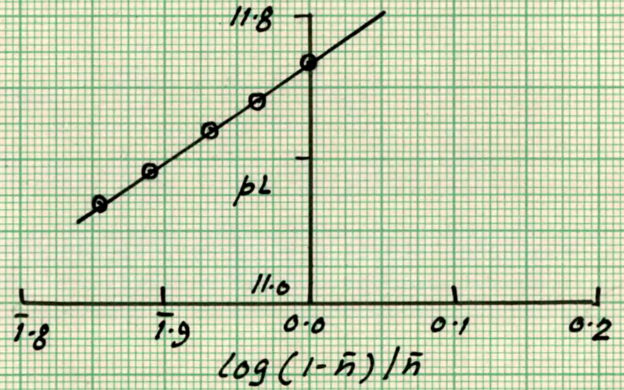


Table II C-3.0 : Proton and metal ligand stability constants of tridentate Schiff bases - 30°C.

Ligand	$P_{K_1}^{H}$	$P_{K_2}^{H}$	logK$_1$ Cu(II)	logK$_1$ Ni(II)
HEA	10.28	8.60	14.26 ± 0.02	10.34 ± 0.06
HEBA	10.53	8.71	14.59 ± 0.05	10.39 ± 0.05
HPA	10.66	8.76	15.03 ± 0.03	11.08 ± 0.07
HPBA	10.84	8.89	15.11 ± 0.05	11.55 ± 0.05

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