CHAPTER TWO

BINARY METAL-DIAMINE SYSTEMS

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

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

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

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

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

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 a competition between the hydrogen ion and the metal ion to combine with 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 the average number of protons bound per not complex bound ligand. If the total concentration of ligand is T_L°, and that of metal ion is M, the concentration of 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 the solution in the form of undissociated molecule H_2L and the ions HL^- and L^{2-}.

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

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

$$-\log L = pL = \log\left[\frac{1 + {}^{P}K_1^H\left(\frac{1}{\text{antilog } B}\right) + {}^{P}K_1^H.\,{}^{P}K_2^H\left(\frac{1}{\text{antilog } B}\right)^2}{T_L^\circ - \bar{n}.T_M^\circ} \cdot \frac{V^\circ + V''}{V^\circ}\right] \qquad (2.2)$$

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 $\log K_2$, respectively. The values are, however, not very precise. The plots of $\bar{n}$ against pL give the formation curves. Various computations of the $\bar{n}$ and pL values have been attempted to get the precise values of the formation constants. Amongst them the method of least square[2,3] is supposed to be most precise and has been used in the present study of metal diamine chelates.

Study of the binary systems containing Cu(II) or Ni(II) and diamines have been carried earlier. The effect of steric hindrance on the chelating tendencies of diamines with $Cu(II)$ and $Ni(II)$ ions has been studied by Basolo and Murmann.[4-6] The stability constants of the complexes formed by N-substituted diamines with $Cu(II)$, $Ni(II)$ and $Zn(II)$ ions have been determined by Calvin-Bjerrum technique.[7] Irving and coworkers[8] have studied the influence of ring size upon the stabilities of metal chelates containing ethylenediamine, propylenediamine or 1,3-diaminopropane. The complex ions formed by $Hg(II)$ ion with three polyamines were investigated by a polarographic method.[9] The successive formation constants of complexes of $Cu(II)$, $Ni(II)$, $Co(II)$ and $Zn(II)$ ions with 1,3-diaminopropane have been studied.[10] Fernelius[11] determined the formation constants and free energy, enthalpy and entropy changes involved in the formation of complexes of N-substituted amines with different metal ions. Martell and coworkers[12] have determined stability constants of complexes of $Cu(II)$ ion with diamines. A potentiometric method has been used to study the effect of $NaClO_4$ on the acid dissociation constants of propylenediamine and the formation constants of its $Zn(II)$ and $Cu(II)$ complexes.[13,14] The complexes $Mn(II)$, $Ni(II)$ and $Zn(II)$ with some symmetrically substituted en have been studied and formation constants values have been determined.[15] A comparative study of the basic strength of N-substituted en and alkanol substituted amines has been carried out.[16] Formation constant values of the complexes of N-N'-dimethyl en with $Cu(II)$ and $Ni(II)$

have been determined by Nasanen and coworkers.[17] The preparation of a series of $Zn(NO_2)_2$ complexes with amines has been reported.[18] The formation of complex between Ni(II) and en was studied spectrophotomatrically and the effect of pH on the nature of the reaction and stability of the complex formed was observed.[19] The complex $[Co(NO_2)_2L_2]$ I where L = N-N'-dimethyl en has been prepared.[20] Reactions of tris(acetylacetonato)Mn(II) and bis(acetylacetonato)Mn(II) with ethylenediamine and pther primary amines have been studied.[21] Steric hindrance in the complex formation of Cd(II) with N-methyl substituted en has been reported.[22] PMR spectra of Cu(II) complex of en has been recorded.[23] Effect of ionic strength on the stability of Co(III) complexes of hexamine tris (en) and tris (pn) have been studied.[24] The stability constants of the 1:1 and 1:2 outer sphere complexes of $[Coen_3]^{3+}$ and $[Copn_3]^{3+}$ with F^-, Cl^- and Br^- have been studied.[25] The stability constants of the mixed ligand complexes of the type Cd(en)X where X = chloride, Br^-, I^-, $S_2O_3^{2-}$, SCN^- were studied by pH metric and potentiotric methods.[26] Migel[27] used polarographic method to study complexes of Cu(II) with ethylenediamine, diethylenetriamine and triethylenetetraamine in water-ethanol solution.

It is observed that the diamine complexes of Ni(II) and Cu(II) have not been studied by using Irving-Rossotti titration technique. Since such values are required for comparison with the ternary complexes, studied in the later chapter, the studies of ethylenediamine, propylenediamine, 1,3-diaminopropane, N-methyl en, N-ethyl en, N-N'-dimethyl en, N-N-dimethyl en and N-N-diethyl en complexes of Ni(II), Cu(II) have been carried out in the present chapter.

Experimental :

Irving-Rossotti titration technique[28] was employed for the determination of the proton ligand and metal ligand formation constants in solution. This technique involves the measurement of pH, which was carried out using a glass calomel electrode and pH meter combination. All the ligands and metals are freely soluble in water and hence water was used as solvent throughout the investigation of these systems.

(a) Materials and purification :-

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

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

Diamines (Fluka, pure), perchloric acid (Baker, analysed reagent, N.J.), sodium perchlorate (Fluka, pure), sodium hydroxide (S.Merck, A.R.), nickel carbonate (supplied by Canning and Co., Birmingham-18), copper carbonate (E.Merck, G.R.), were used.

(b)(1) Oxalic acid : Standard oxalic acid solution of strength 0.5N was prepared by dissolving the required amount of the sample (BDH, A.R.) in conductivity water and making upto required volume.

(2) Sodium hydroxide : 50 gms. of sodium hydroxide was dissolved in 500 ml. conductivity water in a well corked pyrex flask and was kept for two days. The clear supernatant liquid was filtered rapidly through sintered glass crucible of porosity G-4 using vacuum pump into another well cleaned 500 ml. measuring flask. It was then diluted to 500 ml., shaken well and titrated against standard 0.5 N oxalic acid solution using phenolphthalein as an indicator. Thus the strength of the sodium hydroxide solution was determined and also checked pH metrically. From this standard sodium hydroxide solution, solution of required normality was prepared by proper dilution. Care was taken to keep the sodium hydroxide solution free from atmospheric carbondioxide.

(3) Sodium perchlorate solution : The required quantity of sodium perchlorate (A.R.Fluka) was weighed and dissolved in 500 ml. of conductivity water to prepare 1M solution.

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

(5) Metal salt solution : In order to avoid the complexing tendencies of the anion, the perchlorate of nickel was prepared by refluxing its carbonate with perchloric acid till an excess of metal carbonate was left. The filtrate was a neutral solution of nickel perchlorate. In case of the preparation of copper perchlorate, however, weighed quantity of copper carbonate was dissolved in known excess of perchloric acid. This is to avoid the hydrolysis of Cu(II). The amounts of metal ions present in the above perchlorate solutions were estimated. From these stock

solutions, 0.02M metal perchlorate solutions were prepared by proper dilution.

(6) Solutions of complexing agents : A definite volume of diamines were diluted with conductivity water to obtain approximate 0.5M solution of diamines in 100 ml. The exact strength were found out by titrating against standard acid. From these standard solutions, solutions of required concentrations were prepared by proper dilution.

(C) Apparata : All glassware used were of pyrex glass. The micro burette was calibrated to 0.01 by the method described by Vogel.[29] The other measuring vessels as micro-pipettes, measuring flasks of various capacities, pipettes etc. were calibrated by using a standard burette.

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

(e) Details of Irving-Rossotti titration technique : The titration cell was a pyrex beaker fitted with a perspex cover with three holes, through which were admitted the electrode, burette tip and glass stirrer. The tip of the burette was kept in contact with the solution and positioned as near to the stirrer as possible to avoid local concentration of alkali. In all three solutions were prepared : (1) Perchloric acid, (2) perchloric acid and ligand and (3) perchloric acid + ligand + metal. The total volume of 50 ml.

was maintained by the addition of conductivity water. Initially ionic strength of the solution was raised to 0.2M in all the cases by the addition of the required amount of the neutral salt i.e. sodium perchlorate. The solutions for the titrations were prepared as shown below :

1. 0.05M $HClO_4$ + 0.02M ligand + 0.130M $NaClO_4$
2. 0.05M $HClO_4$ + 0.02M ligand + 0.002M nickel perchlorate + 0.128M $NaClO_4$.
3. 0.05M $HClO_4$ + 0.02M ligand + 0.002M copper perchlorate + 0.128M $NaClO_4$.
4. 0.05M $HClO_4$ + 0.150M $NaClO_4$.

The titration beakers containing above solutions were kept for 20 minutes in the waterbath in order to allow them to attain that temperature (30°C).

The ratio of the metal salt to ligand was maintained at 1:10 in all the metal titrations so as to satisfy the highest possible coordination number of the metal ions studied. After addition of each portion of alkali, pH was noted. The highest reading which remains steady was recorded in all the cases. The titration data and curves are given in tables II 1.1 to II 1.8 and in figs. II.1 to II.8.

As seen in the Irving-Rossotti titration curves (figs. II.1 to II.8), at low pH the ligand titration curve, shows higher values of pH than the acid titration curve indicating that it contains less number of titratable hydrogen ions. This is due to the formation of the species $NH_3^+RNH_3^+$. As the pH increases, ligand curve tries to merge with the acid curve due to the formation of $NH_3^+RNH_2$ and finally NH_2RNH_2.

The association of proton with diamines takes place in two stages :

$$NH_2.R.NH_2 + H^+ \xrightleftharpoons{K_1^H} NH_2.R.NH_3^+$$

$$NH_2.R.NH_3^+ + H^+ \xrightleftharpoons{K_2^H} NH_3^+.R.NH_3^+$$

The metal titration curves (2) and (3) show lower pH value for the same amount of alkali than the ligand titration curve (1) due to the liberation of protons from NH_3^+ after coordination. Thus $\bar{n}$ factor can be computed from the difference in the volume of alkali required to produce the same pH in the metal + ligand and ligand titrations. The reaction takes place as follows :

$$M^{2+} + LH_2^{2+} \rightleftharpoons ML^{2+} + 2H^+ \qquad 2H^+ + 2OH^- \rightleftharpoons 2H_2O$$

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

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

$$\bar{n}_H = \frac{(V'-V'')\ (N + E^\circ)}{(V^\circ + V').T_L^\circ} + Y \qquad (2.3)$$

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

V° = the initial volume of solutions.

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

N = the concentration of alkali

E° = the initial concentration of mineral acid

T_L° = the initial total ligand concentration

Y = number of replacable hydrogens from ligand.

The values of proton ligand stability constants have been obtained by linear plot of pH against log $\bar{n}_H/1-\bar{n}_H$. At each point on the straight line pH - log $\bar{n}_H/1-\bar{n}_H = K^H$. K_1^H and K_2^H values were obtained in the range $\bar{n}_H$ 0 to 1 and 1 to 2, respectively, and have been represented in the table II 4.0. The details of intermediate stages of calculations and graphs have not been given to economise space.

(II) Calculation of metal ligand formation constants :

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

$$\bar{n} = \frac{\left[(V''' - V'')\left\{N + E^\circ + T_L^\circ\,(Y - \bar{n}_H)\right\}\right]}{(V^\circ + V'').\bar{n}_H.T_M^\circ} \qquad (2.4)$$

where T_M° = initial total metal ion concentration,

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

(III) Calculation of pL :

For the calculation of pL, the equation (2.2) was used. The pL values calculated have been recorded in tables II 2.1a to II 2.8a and II 2.1b to II 2.8b. The values of $\bar{n}$ have an accuracy of $\pm$ 0.01 depending on the burette precision and the values of pL are significant up to $\pm$ 0.05 depending upon the readability of the pH scale.

At $\bar{n}$ = 0.5 and 1.5 pL values correspond to log K_1 and log K_2, respectively. In cases where $K_1/K_2 > 10^{2.5}$, the above method is used. However, in these cases also determination of formation constants from pL at one point may involve experimental error.

In such cases, however, the formation functions in the two regions of formation of ML_1 and ML_2 reduce to the following form :

$$\bar{n} + (\bar{n} - 1)K_1 (L) = 0 \quad \text{and}$$

$$\bar{n} + (\bar{n} - 2)K_2 (L)^2 = 0$$

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 two ranges $\bar{n} > 0 < 1$ and $\bar{n} > 1 < 2$ have been shown in figs. II 11, II 14 to II 16, II 22 to II 24. The values of log K_1 and log K_2 can be calculated, respectively, at each point on straight lines corresponding to the two regions of $\bar{n}$ by using the following relationship[30]:

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

The average of all these values was obtained and the deviation of each individual value from the average value was calculated. The average values of log K_1 and log K_2 with mean deviation have been presented in tables II 3.3a, II 3.6a to II 3.8a and II 3.6b to II 3.8b. The method, described above, has following advantages :

(1) The values of log K_1 is not obtained only from one point ($\bar{n}$ = 0.5 or 1.5) and the possibility of experimental error is eliminated. (2) The points on the straight lines 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.

In cases where log K_1 / log K_2 $< 10^{2.5}$, it is best to calculate the formation constants using least square technique. The plots of $\bar{n}$ against pL in the present study have been shown in figs. II 9, II 10, II 12, II 13 and II 17 to II 21. They do not show flattening at $\bar{n} = 1$ indicating that the spreading factor in the formation of the first and second step of metal ligand complexes is not high and hence least square method is applicable.

It is seen from equation (2.0) that the above approximate method need not be used, if N equations, of the type referred in equation (2.0), are available for the system with ML_n as the highest possible complex.

In the cases of systems with ML_2 as the highest complex,

$$\bar{n} + (\bar{n}-1)\,K_1\,[L] + (\bar{n}-2)\,K_1.K_2\,[L]^2 = 0 \qquad (2.5)$$

The above equation may be rearranged as follows :

$$\frac{\bar{n}}{(\bar{n}-1)\,[L]} = - \frac{(2-\bar{n})\,[L]}{(\bar{n}-1)} \cdot \beta_2 - K_1 \qquad (2.6)$$

The above equation is wellknown for a straight line of which the slope is $\beta_2(K_1.K_2)$. But, since the term $[L]$ varies over several powers of ten , it is difficult to plot

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

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

$$\Sigma Y = K.a_0 + a_1 \Sigma X$$

$$\Sigma XY = a_0 \Sigma X + A_1 \Sigma X^2 \qquad (2.7)$$

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 (2.7) gave mean value for $\log K_2$. Further, the mean value of K_1 was fitted into equation (2.6) and then individual values from the average values were determined. From the sum of individual deviation the average of these deviations,i.e. mean deviation, was calculated. The calculations and precise values of first and second formation constants obtained by this method have been tabulated in tables II 3.1a, II 3.2a, II 3.4a, II 3.5a, II 3.1b to II 3.5b.

The average values of $\log K_1$ and $\log K_2$ with mean deviation obtained by least square or linear plot method, have been represented in table II 5.0.

The diamines are characterised by two K^H values. Propylenediamine and 1,3-diaminopropane show higher values of K^H than that of ethylenediamine. This is because of the positive inductive effect of the $-CH_3$ group. In case of propylenediamine the $-CH_3$ group is nearer to one $-NH_2$ and farther from the other. As a result of it K_1^H value shows an increase whereas K_2^H remains nearly same as in ethylenediamine. In 1,3-diaminopropane the added CH_3 group has equal effect on both the $-NH_2$ and hence both K_1^H and K_2^H values show increase.

Substitution of a proton on NH_2 by alkyl group also produces a small increase in basic strength. This is because of the positive inductive effect of the alkyl group. The electron release by alkyl group increases the electron density on nitrogen and hence increases its affinity for a proton. The proton ligand stability constant values are in order N ethyl en $>$ N methyl en $>$ en. The introduction of second alkyl group over the same nitrogen atom, however, lowers the value of K_1^H and K_2^H. This can be explained as in case of trialkyl amine.[31] Though there is an increase in the electron density over the nitrogen atom with the increase in the number of alkyl groups, the possibility of the solvation of the protonated cation and hence its stability goes on decreasing with the substitution of hydrogen by alkyl groups. A second alkyl group placed symmetrically over the other nitrogen atom has a slight effect on the P_K^H values of the first NH_2. Thus in case of symmetrical N-N'-dimethyl en the values of K_1^H and K_2^H are very close to those of unsubstituted ethylenediamine.

Bidentate ligand ethylenediamine forms stronger complexes with all metals than those formed with two molecules of ammonia or two molecules of primary monoamines. $\text{Log}K_{ML}^M$ values are lower for ethylenediamine complexes than corresponding propylenediamine complexes. This is in accordance with the basicity of the ligand. However, 1,3-diaminopropane forms less stable complexes with Ni(II) and Cu(II) as compared to en and pn though its basic strength is more. This is because 1,3-diaminopropane forms less stable six membered ring chelates while ethylenediamine and propylenediamine form more stable five membered ring chelates. Though N-methyl and N-ethyl ethylenediamine are more basic than en, there is a decrease in the stability of their 1:1 and 1:2 metal complexes. This is because of steric hindrance. The base strengthening effect of alkyl substitution is necessarily accompanied by an increase in molar volume and steric hindrance between amine molecules coordinated to a metal ion and also between amine molecule and coordinated water. This tends to reduce the stabilities of such metal complexes.

The effect is more pronounced in N-ethyl en than in N-methyl en. Disubstitution produces more steric hindrance resulting in further decrease in the values of formation constants. The effect is maximum in case of N-N-dimethylethylenediamine, rendering the values of $\log K_1$ minimum. In case of symmetrical N-N'-dimethyl ethylenediamine, the hindrance is comparatively less than in N-N-dimethyl en and hence the values of stability constants of its complexes are slightly higher. Thus the order of the stability constants of the diamine complexes can be explained in terms of basicity and steric factors. The Cu(II) complexes are more stable than Ni(II) complexes as explained in the Irving-William order.

Table II 1.1

$N = 0.5M$ $\quad V^{\circ} = 50$ ml. $\quad \mu = 0.2M$ $\quad t = 30°C.$

$E^{\circ} = 0.05M$ $\quad T_L^{\circ} = 0.02M$ $\quad T_M^{\circ} = 0.002M$

Perchloric acid		Ethylenediamine		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	1.30	0.00	1.90	0.00	1.95	0.00	1.95
1.00	1.40	0.40	2.20	0.40	2.30	0.40	2.30
2.00	1.50	0.60	2.45	0.60	2.65	0.70	2.80
3.00	1.60	0.75	2.95	0.70	3.10	0.80	3.50
4.00	1.85	0.82	3.80	0.80	3.50	0.82	3.90
4.20	2.00	0.84	4.60	0.90	3.80	0.84	4.60
4.50	2.25	0.86	5.10	1.05	4.10	0.86	4.95
4.60	2.40	0.92	5.60	1.20	4.35	0.95	5.25
4.70	2.50	1.00	5.90	1.40	4.70	1.00	5.35
4.80	2.70	1.20	6.25	1.50	4.95	1.20	5.70
4.90	3.25	1.40	6.50	1.60	5.25	1.40	5.95
4.92	3.40	1.60	6.70	1.65	5.55	1.60	6.20
4.94	3.80	1.80	6.85	1.70	5.80	1.80	6.40
4.96	4.70	2.00	7.05	1.80	6.05	2.00	6.66
4.98	6.50	2.30	7.40	2.00	6.40	2.30	6.85
5.00	8.50	2.60	7.70	2.20	6.80	2.60	7.15
5.02	9.20	2.80	8.10	2.60	7.20	2.80	7.35
5.06	9.70	3.00	8.60	2.90	7.55	3.00	7.55
5.10	10.00	3.20	9.05	3.10	7.90	3.20	7.80
5.20	10.55	3.40	9.30	3.20	8.25	3.50	8.45
5.30	10.70	3.80	9.70	3.30	8.60	3.60	8.80
5.40	10.80	4.40	10.10	3.40	8.90	3.80	9.20
5.50	10.90	5.00	10.60	3.80	9.50	4.10	9.60
5.60	11.00			4.40	10.00	4.60	10.00

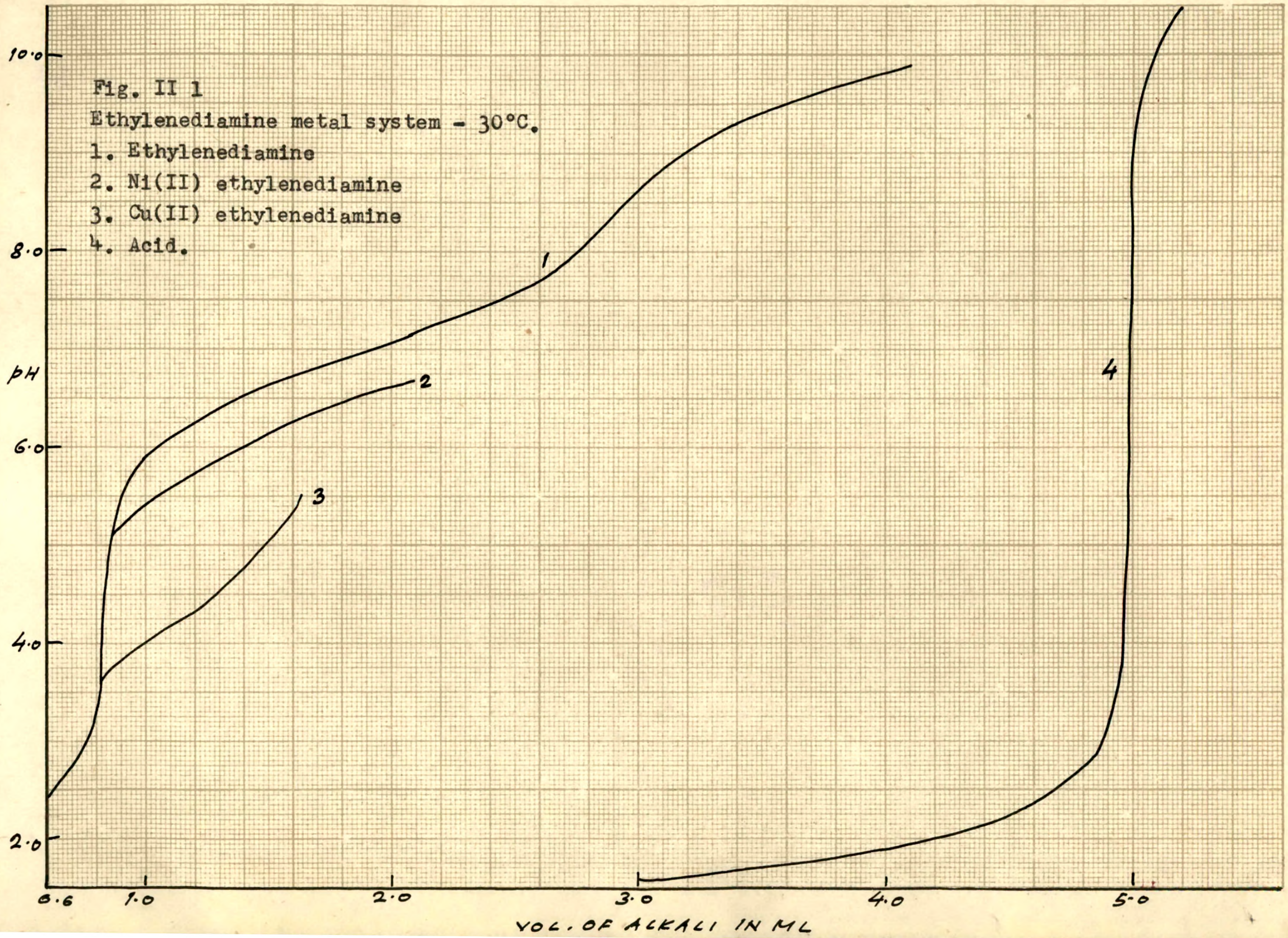


Fig. II 1

Ethylenediamine metal system - 30°C.

1. Ethylenediamine
2. Ni(II) ethylenediamine
3. Cu(II) ethylenediamine
4. Acid.

Table II 1.2

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.05M T°_{L} = 0.02M T°_{M} = 0.002M

Perchloric acid		Propylenediamine		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	1.30	0.00	1.90	0.00	1.95	0.00	1.95
1.00	1.40	0.40	2.20	0.40	2.40	0.40	2.20
2.00	1.50	0.60	2.50	0.60	2.70	0.60	2.50
3.00	1.60	0.70	2.80	0.70	3.10	0.70	2.80
4.00	1.85	0.75	3.05	0.78	3.40	0.78	3.40
4.20	2.00	0.78	3.40	0.90	3.70	0.82	4.30
4.50	2.25	0.82	4.50	1.10	4.00	0.86	4.80
4.60	2.40	0.86	5.10	1.30	4.35	0.90	5.00
4.70	2.50	0.92	5.40	1.40	4.60	1.10	5.40
4.80	2.70	1.00	5.70	1.50	4.90	1.40	5.70
4.90	3.25	1.20	6.05	1.60	5.25	1.70	6.00
4.92	3.40	1.40	6.35	1.70	5.80	2.00	6.30
4.94	3.80	1.80	6.70	1.80	6.05	2.40	6.70
4.96	4.70	2.20	7.05	2.00	6.40	2.60	6.90
4.98	6.50	2.50	7.40	2.20	6.80	2.80	7.10
5.00	8.50	2.70	7.75	2.60	7.20	3.00	7.40
5.02	9.20	2.80	8.00	2.90	7.55	3.20	7.70
5.06	9.70	2.90	8.25	3.10	7.90	3.40	8.10
5.10	10.00	3.00	8.55	3.20	8.25	3.50	8.45
5.20	10.55	3.10	8.80	3.30	8.60	3.60	8.80
5.30	10.70	3.30	9.20	3.40	8.90	3.80	9.25
5.40	10.80	3.80	9.65	3.80	9.50	4.00	9.65
5.50	10.90	4.40	10.05	4.40	10.00	4.40	9.95
5.60	11.00	5.00	10.60			5.00	10.55

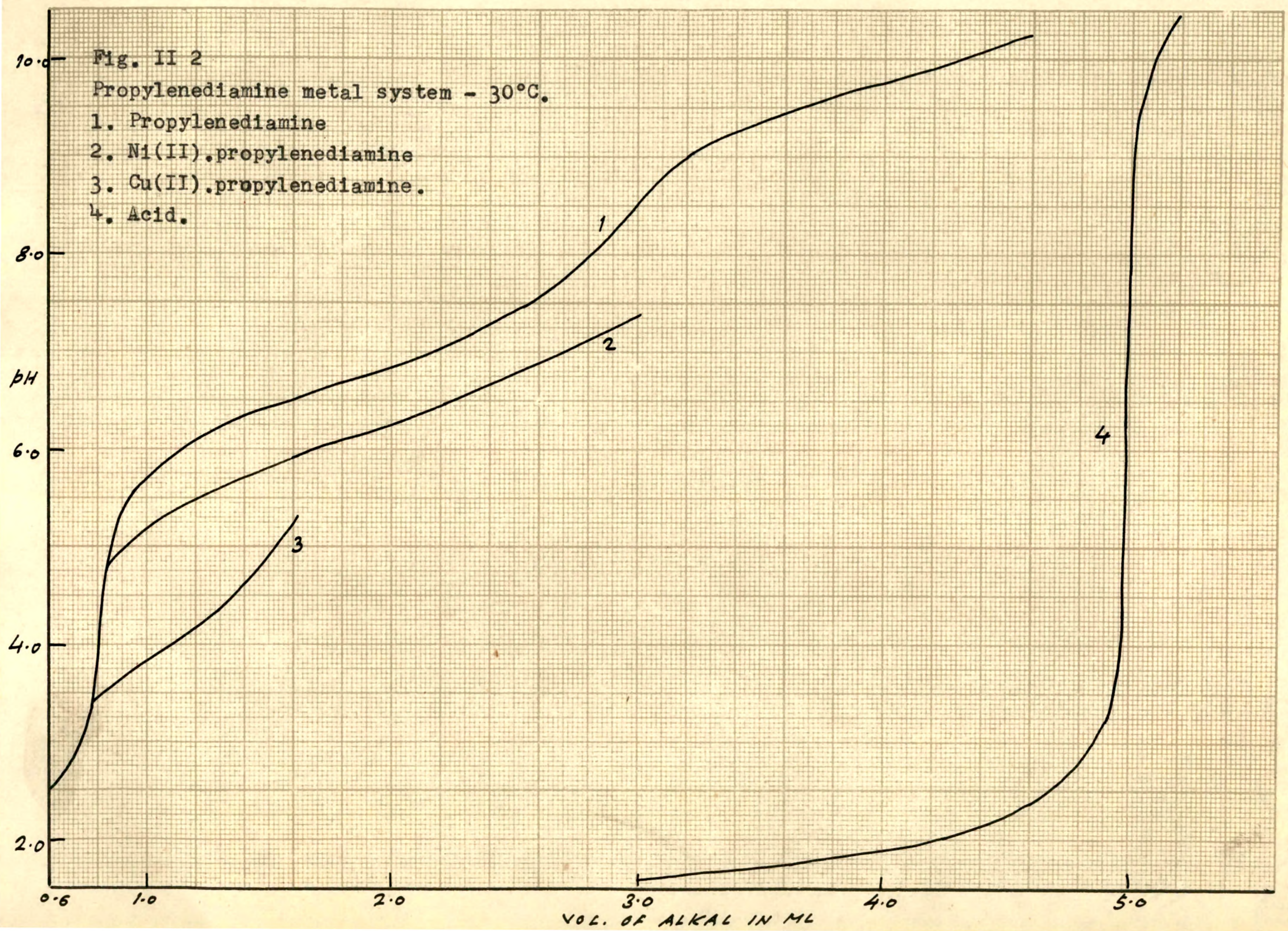


Fig. II 2

Propylenediamine metal system - 30°C.

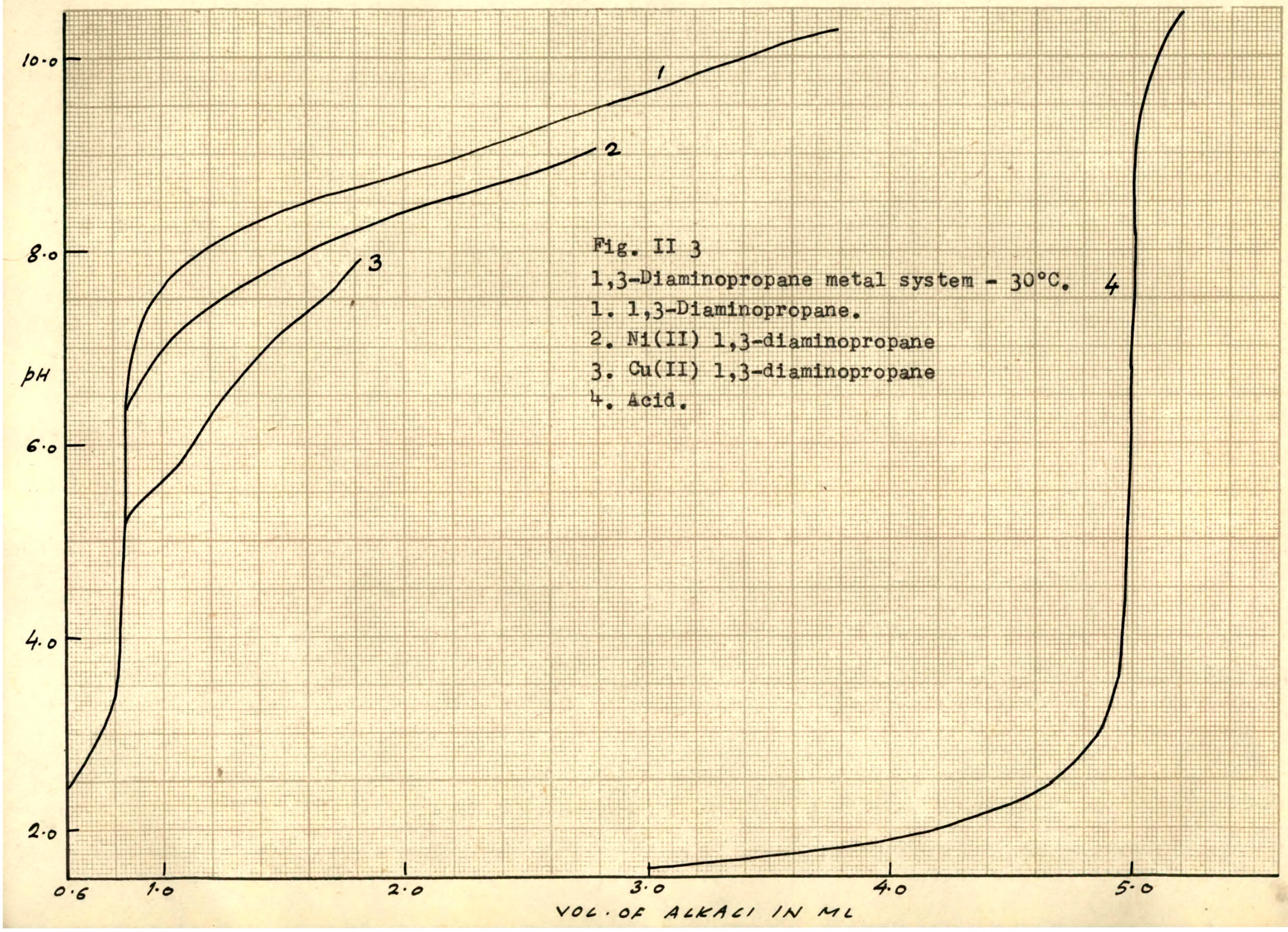
1. Propylenediamine
2. Ni(II).propylenediamine
3. Cu(II).propylenediamine.
4. Acid.

Table II 1.3

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.05M T_L° = 0.02M T_M° = 0.002M

Perchloric acid		1,3-diaminopropane		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	1.30	0.00	1.90	0.00	1.90	0.00	1.90
1.00	1.40	0.40	2.20	0.40	2.25	0.40	2.20
2.00	1.50	0.70	2.75	0.60	2.65	0.60	2.50
3.00	1.60	0.76	3.10	0.70	3.25	0.70	2.75
4.00	1.85	0.80	3.40	0.75	4.70	0.80	3.55
4.20	2.00	0.82	4.25	0.80	5.10	0.82	4.70
4.50	2.25	0.84	6.10	0.90	5.40	0.84	6.15
4.60	2.40	0.86	6.75	1.00	5.65	0.86	6.40
4.70	2.50	0.90	7.10	1.10	5.90	0.95	6.85
4.80	2.70	0.96	7.45	1.20	6.30	1.00	7.05
4.90	3.25	1.04	7.75	1.30	6.65	1.20	7.45
4.92	3.40	1.20	8.05	1.40	6.90	1.40	7.75
4.94	3.80	1.40	8.30	1.60	7.35	1.60	8.00
4.96	4.70	1.60	8.50	1.70	7.60	1.80	8.25
4.98	6.50	2.00	8.80	1.80	7.90	2.00	8.40
5.00	8.50	2.40	9.15	2.00	8.20	2.40	8.70
5.02	9.20	2.80	9.50	2.20	8.45	2.80	9.05
5.06	9.70	3.00	9.65	2.40	8.65	3.00	9.20
5.10	10.00	3.20	9.80	2.60	8.85	3.20	9.40
5.20	10.55	3.40	10.00	2.80	9.05	3.40	9.65
5.30	10.70	3.60	10.15	3.20	9.50	3.62	9.90
5.40	10.80	4.00	10.40	3.60	9.90	4.00	10.15
5.50	10.90	4.40	10.60	4.00	10.25	4.40	10.50
5.60	11.00	5.00	10.90	4.40	10.50	5.00	10.85



10·0
8·0
pH
6·0
4·0
2·0
0·6
1·0
2·0
3·0
4·0
5·0
VOL. OF ALKALI IN ML
1
2
3
4
Fig. II 3
1,3-Diaminopropane metal system - 30°C.
1. 1,3-Diaminopropane.
2. Ni(II) 1,3-diaminopropane
3. Cu(II) 1,3-diaminopropane
4. Acid.

Table II 1.4

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.05M T_L^o = 0.02M T_M^o = 0.002M

Perchloric acid		N-Methyl en		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	1.30	0.00	1.90	0.00	1.90	0.00	1.90
1.00	1.40	0.20	2.00	0.20	2.05	0.40	2.10
2.00	1.50	0.60	2.45	0.40	2.30	0.60	2.40
3.00	1.60	0.76	2.90	0.60	2.60	0.75	3.00
4.00	1.85	0.80	3.40	0.70	2.90	0.80	3.50
4.20	2.00	0.82	4.40	0.78	3.45	0.82	4.10
4.50	2.25	0.84	4.80	0.86	3.85	0.84	4.70
4.60	2.40	0.90	5.40	1.00	4.15	0.88	5.05
4.70	2.50	0.95	5.65	1.20	4.55	0.95	5.25
4.80	2.70	1.00	5.90	1.30	4.80	1.00	5.40
4.90	3.25	1.20	6.30	1.40	5.00	1.20	5.80
4.92	3.40	1.40	6.55	1.60	5.40	1.40	6.05
4.94	3.80	1.80	6.90	1.70	5.65	1.50	6.15
4.96	4.70	2.00	7.10	1.80	5.95	1.60	6.25
4.98	6.50	2.20	7.25	2.00	6.45	1.70	6.35
5.00	8.50	2.40	7.50	2.20	6.70	1.80	6.50
5.02	9.20	2.60	7.85	2.40	7.00	1.90	6.55
5.06	9.70	2.80	8.20	2.80	7.35	2.00	6.65
5.10	10.00	2.90	8.50	3.00	7.70	2.20	6.80
5.20	10.55	3.00	8.85	3.10	7.95	2.40	7.00
5.30	10.70	3.20	9.25	3.20	8.25	2.60	7.20
5.40	10.80	3.60	9.65	3.30	8.70	3.00	7.65
5.50	10.90	4.20	10.10	3.40	9.00	3.10	7.90
5.60	11.00	4.80	10.55	3.70	9.50 (ppts)	3.20	8.15 (ppts)

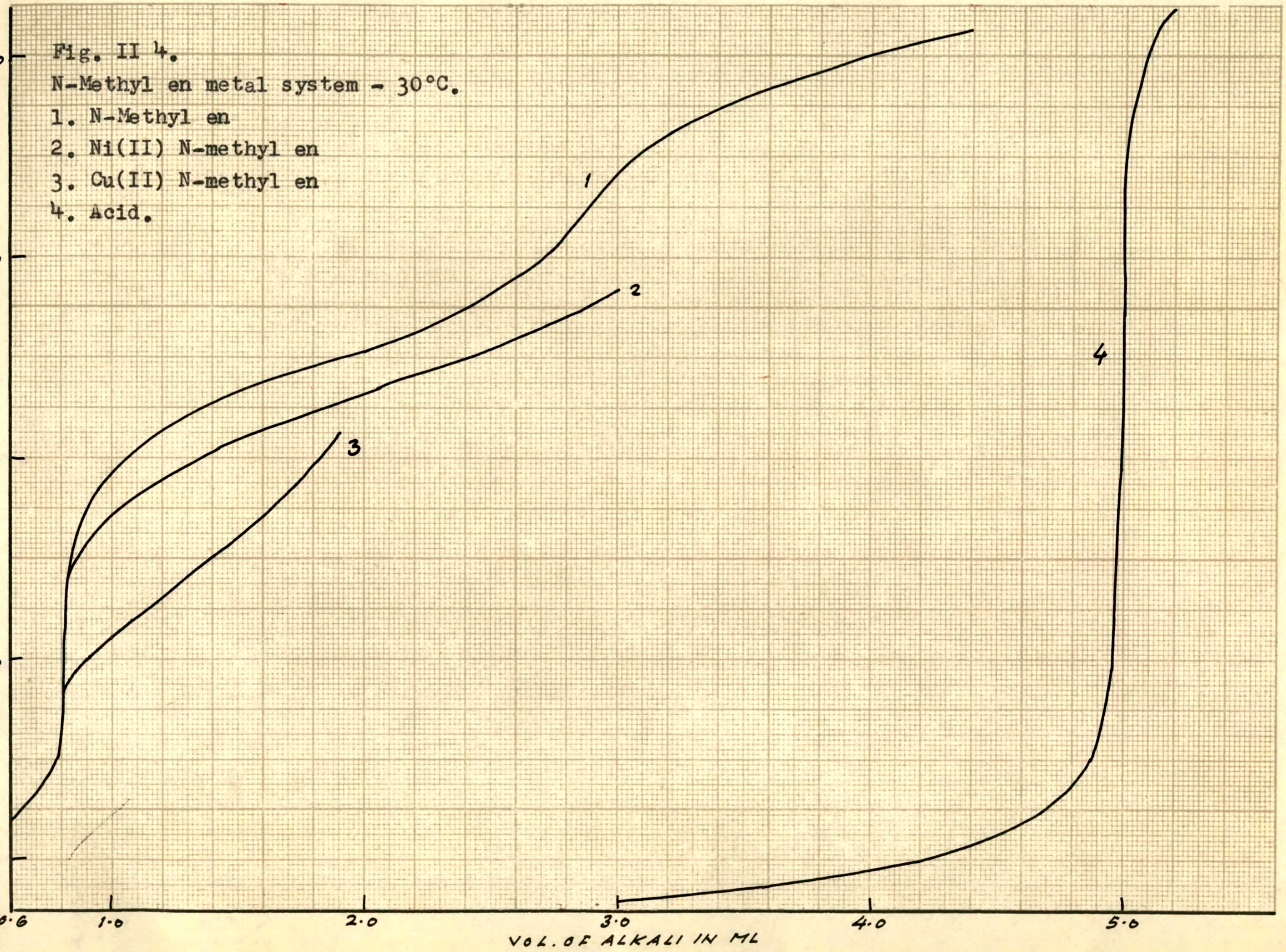


Fig. II 4.
N-Methyl en metal system - 30°C.
1. N-Methyl en
2. Ni(II) N-methyl en
3. Cu(II) N-methyl en
4. Acid.
pH
10.0
8.0
6.0
4.0
2.0
0.6
1.0
2.0
3.0
4.0
5.0
VOL. OF ALKALI IN ML
1
2
3
4

Table II 1.5

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.05M T°_{L} = 0.02M T°_{M} = 0.002M

Perchloric acid		N-Ethyl en		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	1.30	0.00	1.90	0.00	1.95	0.00	1.90
1.00	1.40	0.20	2.10	0.20	2.10	0.20	2.00
2.00	1.50	0.40	2.25	0.60	2.60	0.60	2.50
3.00	1.60	0.60	2.55	0.70	3.00	0.75	3.00
4.00	1.85	0.70	2.80	0.76	3.55	0.80	3.50
4.20	2.00	0.76	3.10	0.78	3.80	0.82	3.90
4.50	2.25	0.80	3.60	0.82	4.00	0.84	4.60
4.60	2.40	0.82	4.20	0.90	4.30	0.86	5.00
4.70	2.50	0.86	5.20	1.00	4.50	0.90	5.35
4.80	2.70	0.90	5.50	1.20	4.90	1.00	5.65
4.90	3.25	1.00	5.95	1.30	5.10	1.10	5.85
4.92	3.40	1.10	6.20	1.40	5.35	1.20	6.00
4.94	3.80	1.20	6.35	1.50	5.55	1.40	6.25
4.96	4.70	1.40	6.65	1.60	5.80	1.60	6.45
4.98	6.50	1.60	6.90	1.80	6.20	1.80	6.65
5.00	8.50	1.80	7.10	2.00	6.50	2.00	6.85
5.02	9.20	2.00	7.25	2.20	6.80	2.20	7.00
5.06	9.70	2.40	7.65	2.40	7.00	2.40	7.15
5.10	10.00	2.80	8.35	2.60	7.25	2.60	7.35
5.20	10.55	2.90	8.65	2.80	7.50	2.80	7.50
5.30	10.70	3.10	9.20	3.00	7.80	3.00	7.75
5.40	10.80	3.40	9.65	3.20	8.30	3.20	8.15
5.50	10.90	3.80	10.00	3.40	9.00	3.30	8.50
5.60	11.00	4.40	10.45	3.60	9.45 (ppts)	3.40	8.85 (ppts).

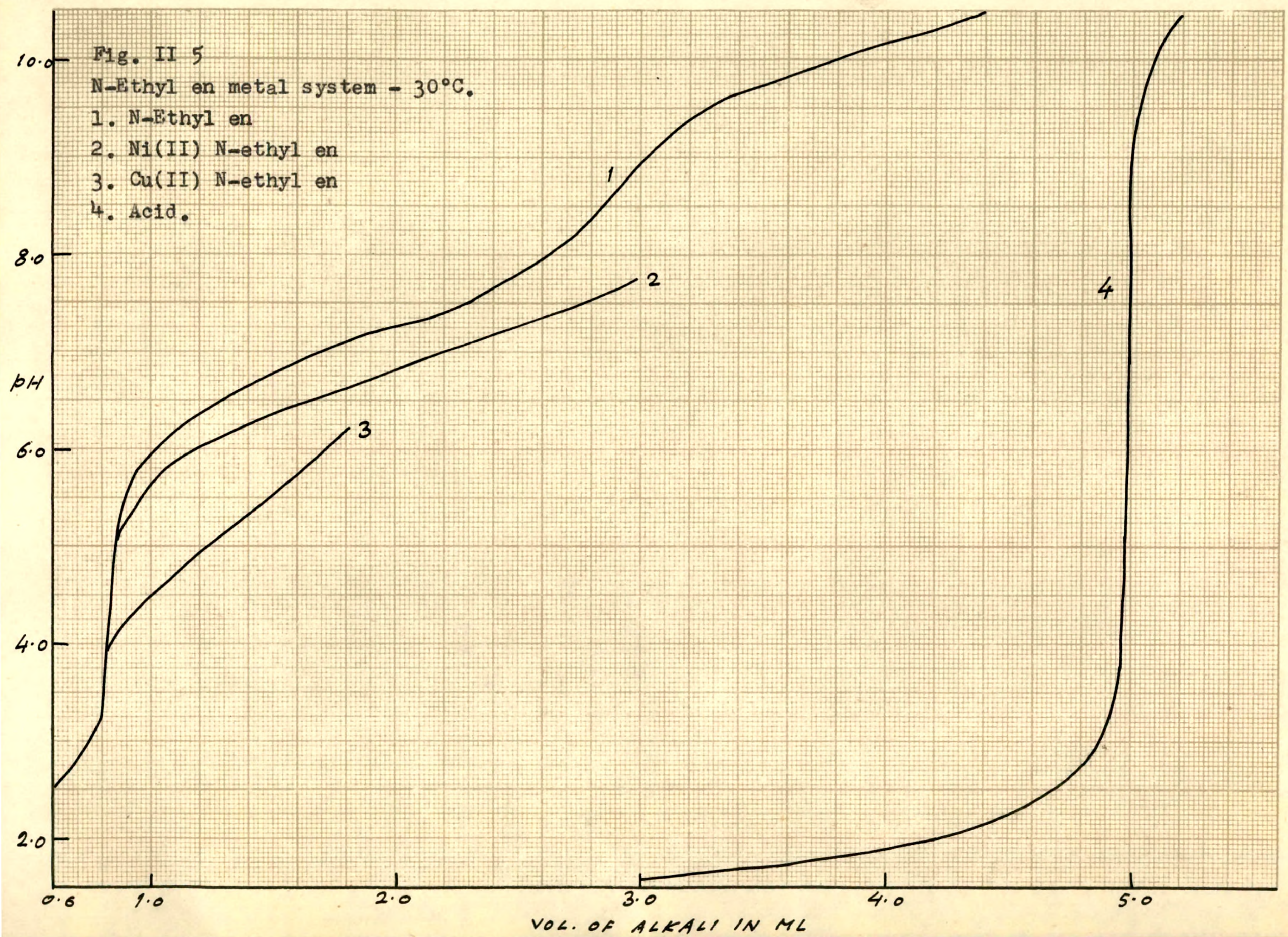


Fig. II 5
N-Ethyl en metal system - 30°C.
1. N-Ethyl en
2. Ni(II) N-ethyl en
3. Cu(II) N-ethyl en
4. Acid.
10.0
8.0
pH
6.0
4.0
2.0
0.6
1.0
2.0
3.0
4.0
5.0
VOL. OF ALKALI IN ML
1
2
3
4

Table II 1.6

N = 0.5M   V° = 50 ml. μ = 0.2M   t = 30°C.

E° = 0.05M T°_L = 0.02M T°_M = 0.002M

Perchloric acid		N-N'-Dimethyl en		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	1.30	0.00	1.95	0.00	1.90	0.00	1.95
1.00	1.40	0.40	2.20	0.20	2.05	0.40	2.30
2.00	1.50	0.60	2.45	0.40	2.30	0.60	2.55
3.00	1.60	0.70	2.75	0.60	2.70	0.70	2.80
4.00	1.85	0.80	3.25	0.70	3.25	0.80	3.40
4.20	2.00	0.82	3.60	0.75	3.60	0.82	3.65
4.50	2.25	0.86	4.10	0.86	4.00	0.86	4.10
4.60	2.40	0.90	4.60	1.00	4.30	0.88	4.45
4.70	2.50	0.95	5.15	1.20	4.75	0.92	4.95
4.80	2.70	1.00	5.50	1.30	5.15	1.00	5.35
4.90	3.25	1.10	5.90	1.40	5.50	1.10	5.60
4.92	3.40	1.20	6.15	1.60	5.85	1.30	5.90
4.94	3.80	1.40	6.45	1.80	6.15	1.50	6.20
4.96	4.70	1.80	6.85	2.00	6.45	1.70	6.45
4.98	6.50	2.00	7.05	2.20	6.80	2.00	6.75
5.00	8.50	2.40	7.45	2.60	7.25	2.20	6.95
5.02	9.20	2.60	7.70	2.80	7.50	2.40	7.15
5.06	9.70	2.80	8.00	3.00	7.80	2.60	7.30
5.10	10.00	3.00	8.50	3.20	8.10	2.80	7.60
5.20	10.55	3.20	9.00	3.30	8.50	3.20	8.15
5.30	10.70	3.40	9.35	3.40	8.80	3.50	8.75
5.40	10.80	3.60	9.60	3.60	9.30	3.60	9.10
5.50	10.90	4.00	9.90	4.00	9.75	4.00	9.65
5.60	11.00	4.80	10.60	4.40	10.15	4.60	10.20

Fig. II 6

N-N'-Dimethyl en metal system - 30°C.

1. N-N'-Dimethyl en
2. Ni(II) N-N'-dimethyl en
3. Cu(II) N-N'-dimethyl en
4. Acid.

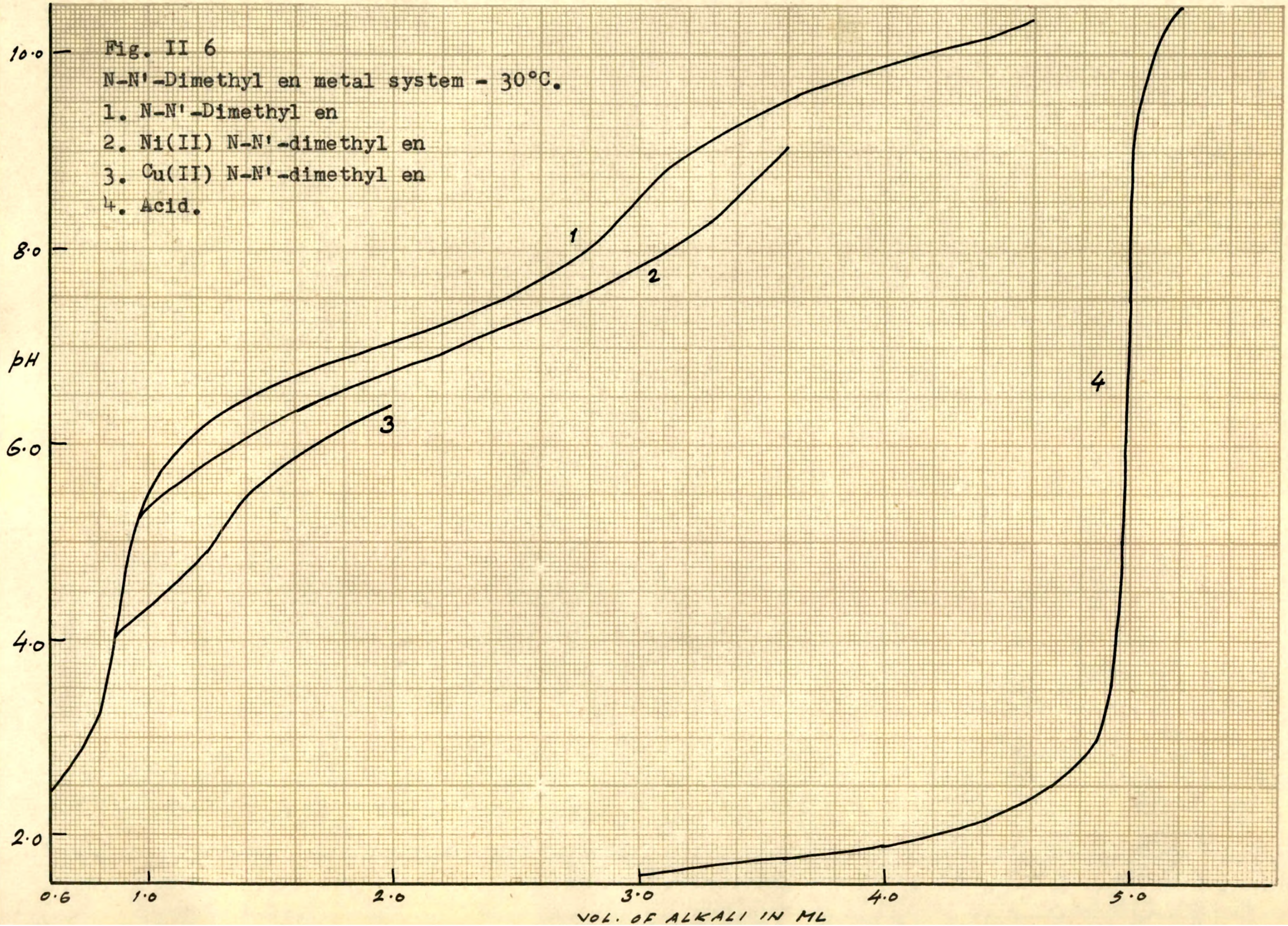


Table II 1.7

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.05M T_L° = 0.02M T_M° = 0.002M

Perchloric acid		N-N-Dimethyl en		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	1.30	0.00	1.90	0.00	1.90	0.00	1.90
1.00	1.40	0.40	2.20	0.40	2.20	0.20	2.00
2.00	1.50	0.60	2.50	0.65	2.80	0.60	2.45
3.00	1.60	0.75	3.00	0.75	3.40	0.70	2.70
4.00	1.85	0.80	3.65	0.80	3.65	0.78	3.10
4.20	2.00	0.82	4.00	0.90	3.95	0.82	3.70
4.50	2.25	0.84	4.40	1.10	4.40	0.86	4.50
4.60	2.40	0.88	4.80	1.30	4.85	0.90	4.85
4.70	2.50	0.96	5.20	1.40	5.15	0.95	5.10
4.80	2.70	1.10	5.55	1.60	5.40	1.20	5.50
4.90	3.25	1.40	5.95	1.80	5.65	1.40	5.75
4.92	3.40	1.80	6.30	2.10	6.00	1.60	5.90
4.94	3.80	2.00	6.50	2.40	6.35	1.80	6.10
4.96	4.70	2.40	6.95	2.60	6.60	2.00	6.30
4.98	6.50	2.60	7.30	2.80	6.85	2.40	6.60
5.00	8.50	2.80	7.75	3.00	7.20	2.70	6.95
5.02	9.20	2.90	8.10	3.10	7.50	3.00	7.40
5.06	9.70	3.00	8.40	3.20	7.85	3.20	7.85
5.10	10.00	3.20	8.85	3.30	8.25	3.30	8.20
5.20	10.55	3.40	9.10	3.40	8.60	3.40	8.50
5.30	10.70	3.80	9.50	3.60	9.00	3.50	8.70
5.40	10.80	4.20	9.80	4.00	9.45	3.60	8.90
5.50	10.90	4.60	10.10	4.50	9.90	3.80	9.15
5.60	11.00	5.00	10.50	5.00	10.55	4.00	9.40

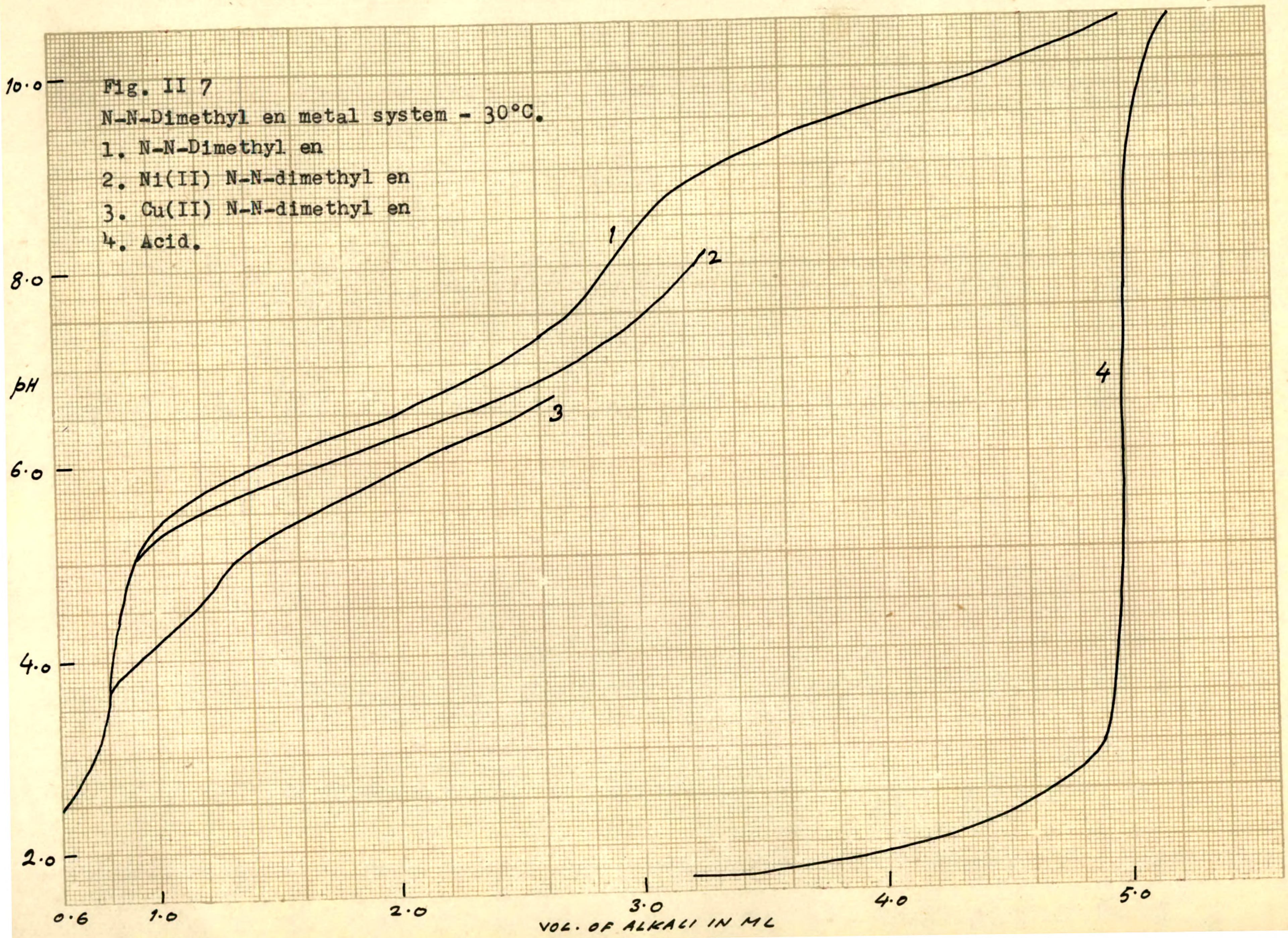


Fig. II 7
N-N-Dimethyl en metal system - 30°C.
1. N-N-Dimethyl en
2. Ni(II) N-N-dimethyl en
3. Cu(II) N-N-dimethyl en
4. Acid.
pH
10·0
8·0
6·0
4·0
2·0
0·6
1·0
2·0
3·0
4·0
5·0
VOL. OF ALKALI IN ML
1
2
3
4

Table II 1.8

N = 0.5M V° = 50 ml. μ = 0.2M t = 30°C.

E° = 0.05M T°_{L} = 0.02M. T°_{M} = 0.002M

Perchloric acid		N-N-Diethyl en		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	1.30	0.00	1.90	0.00	1.90	0.00	1.90
1.00	1.40	0.40	2.20	0.40	2.30	0.40	2.20
2.00	1.50	0.60	2.50	0.60	2.70	0.60	2.50
3.00	1.60	0.70	2.75	0.66	3.00	0.74	3.00
4.00	1.85	0.76	3.10	0.70	3.35	0.78	3.50
4.20	2.00	0.80	3.80	0.74	3.95	0.82	4.25
4.50	2.25	0.84	4.60	0.78	4.30	0.86	4.85
4.60	2.40	0.88	5.20	0.84	4.60	0.90	5.30
4.70	2.50	0.92	5.45	1.00	5.00	0.94	5.60
4.80	2.70	1.00	5.85	1.10	5.25	1.00	5.80
4.90	3.25	1.10	6.20	1.20	5.50	1.10	6.15
4.92	3.40	1.40	6.65	1.30	5.70	1.20	6.30
4.94	3.80	1.60	6.90	1.40	6.00	1.40	6.50
4.96	4.70	1.80	7.10	1.60	6.40	1.60	6.70
4.98	6.50	2.20	7.45	2.00	6.85	2.00	7.05
5.00	8.50	2.50	7.75	2.20	7.00	2.40	7.40
5.02	9.20	2.80	8.25	2.60	7.40	2.60	7.65
5.06	9.70	3.00	8.75	3.00	7.95	2.80	7.90
5.10	10.00	3.10	9.05	3.20	8.40	3.00	8.20
5.20	10.55	3.30	9.35	3.30	8.75	3.10	8.40
5.30	10.70	3.50	9.60	3.40	9.00	3.20	8.65
5.40	10.80	4.00	9.95	3.60	9.40	3.40	9.10
5.50	10.90	4.20	10.10	4.00	9.85	3.80	9.65
5.60	11.00	5.00	10.65	4.40	10.20	4.20	10.00

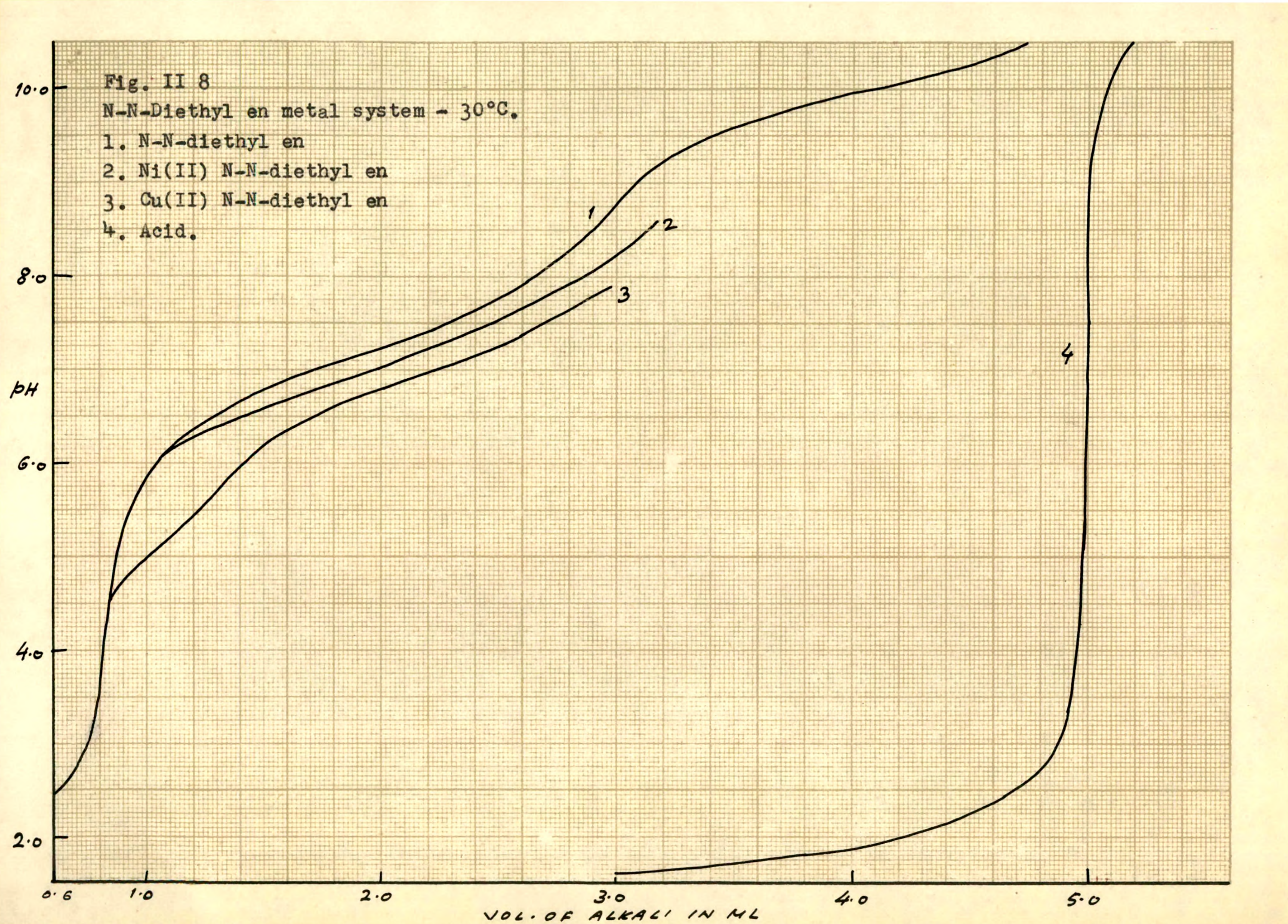


Fig. II 8
N-N-Diethyl en metal system - 30°C.
1. N-N-diethyl en
2. Ni(II) N-N-diethyl en
3. Cu(II) N-N-diethyl en
4. Acid.
10·0
8·0
pH
6·0
4·0
2·0
0·6
1·0
2·0
3·0
4·0
5·0
VOL. OF ALKALI IN ML
1
2
3
4

Table II 2.1a

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
3.90	2.00_0	0.82	0.93	0.11	0.28_7	11.01_9
4.00	2.00_0	0.82	0.98	0.16	0.41_7	10.82_5
4.10	2.00_0	0.82	1.04	0.22	0.57_3	10.63_3
4.20	2.00_0	0.83	1.10	0.27	0.70_4	10.44_0
4.30	2.00_0	0.83	1.17	0.34	0.88_6	10.24_9
4.40	2.00_0	0.83	1.24	0.41	1.07_0	10.05_8
4.50	2.00_0	0.84	1.30	0.46	1.15_3	9.86_5
4.60	2.00_0	0.84	1.34	0.50	1.25_4	9.66_8
4.70	2.00_0	0.84	1.38	0.54	1.35_4	9.47_4
4.80	2.00_0	0.85	1.42	0.57	1.42_9	9.27_8
4.90	2.00_0	0.86	1.47	0.61	1.52_9	9.08_3

Table II 2.2a

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
3.70	2.00_0	0.80	0.90	0.10	0.25_1	11.51_7
3.80	2.00_0	0.80	0.95	0.15	0.37_6	11.32_3
3.90	2.00_0	0.80	1.00	0.20	0.50_1	11.13_0
4.00	2.00_0	0.80	1.07	0.27	0.67_7	10.93_9
4.10	2.00_0	0.81	1.14	0.33	0.82_8	10.74_7
4.30	2.00_0	0.81	1.27	0.46	1.15_0	10.36_3
4.40	2.00_0	0.82	1.31	0.49	1.22_9	10.16_7
4.50	2.00_0	0.82	1.36	0.54	1.35_4	9.97_3
4.60	2.00_0	0.82	1.41	0.59	1.48_0	9.78_0

Table II 2.3a

$\bar{n}_H$, $\bar{n}$, pL data for Cu(II) 1,3-diaminopropane system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.40	2.00_0	0.83	0.91	0.08	0.20_1	10.31_5
5.50	2.00_0	0.83	0.95	0.12	0.30_0	10.12_0
5.60	2.00_0	0.83	0.99	0.16	0.40_1	9.92_5
5.70	2.00_0	0.83	1.03	0.20	0.50_1	9.73_0
5.80	2.00_0	0.83	1.07	0.24	0.60_2	9.53_5
5.90	2.00_0	0.83	1.10	0.27	0.67_7	9.33_9
6.70	2.00_0	0.86	1.31	0.45	1.12_8	7.76_5
6.80	2.00_0	0.87	1.35	0.48	1.20_3	7.57_0
6.90	2.00_0	0.88	1.38	0.50	1.25_3	7.37_4
7.00	2.00_0	0.89	1.42	0.53	1.32_8	7.18_0
7.10	2.00_0	0.90	1.47	0.57	1.42_8	6.98_7
7.20	2.00_0	0.91	1.53	0.62	1.55_2	6.79_6

Table II 2.4a

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.00	2.00_0	0.82	0.92	0.10	0.25_1	11.11_8
4.10	2.00_0	0.82	0.97	0.15	0.36_6	10.92_4
4.20	2.00_0	0.82	1.02	0.20	0.50_1	10.73_0
4.30	2.00_0	0.82	1.06	0.24	0.60_2	10.53_6
4.40	2.00_0	0.82	1.11	0.29	0.72_7	10.34_2
4.50	2.00_0	0.82	1.16	0.34	0.85_3	10.14_9
4.60	2.00_0	0.82	1.21	0.39	0.97_8	9.95_5
4.70	2.00_0	0.83	1.27	0.44	1.10_3	9.76_2
4.80	2.00_0	0.84	1.30	0.46	1.15_3	9.56_5
4.90	2.00_0	0.84	1.36	0.52	1.30_4	9.37_4
5.00	2.00_0	0.85	1.41	0.56	1.40_4	9.18_0
5.10	2.00_0	0.86	1.47	0.61	1.52_9	8.98_7

Table II 2.5a

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.40	2.00_0	0.84	0.94	0.10	0.25_1	10.91_8
4.50	2.00_0	0.84	0.99	0.15	0.37_6	10.72_5
4.60	2.00_0	0.84	1.03	0.19	0.47_6	10.53_0
4.70	2.00_0	0.84	1.08	0.24	0.60_2	10.33_6
4.80	2.00_0	0.84	1.14	0.29	0.72_7	10.14_3
4.90	2.00_0	0.84	1.20	0.36	0.90_3	9.95_2
5.00	2.00_0	0.85	1.25	0.40	1.00_0	9.75_8
5.10	2.00_0	0.85	1.30	0.45	1.12_8	9.56_5
5.30	2.00_0	0.88	1.37	0.49	1.22_8	9.17_2
5.40	2.00_0	0.89	1.42	0.53	1.32_8	8.97_9
5.50	2.00_0	0.90	1.47	0.57	1.42_7	8.78_6
5.60	2.00_0	0.91	1.50	0.59	1.47_7	8.59_1
5.70	2.00_0	0.93	1.55	0.62	1.55_2	8.39_7

Table II 2.6a

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.20	2.00_0	0.88	0.95	0.07	0.17_5	10.41_5
4.25	2.00_0	0.88	0.97	0.09	0.22_5	10.31_8
4.30	2.00_0	0.88	1.00	0.12	0.30_1	10.22_2
4.40	2.00_0	0.89	1.05	0.16	0.40_1	10.02_6
4.50	2.00_0	0.89	1.09	0.20	0.50_1	9.83_2
4.60	2.00_0	0.90	1.13	0.23	0.57_6	9.63_6
5.70	1.96_1	1.04	1.50	0.46	1.17_3	7.48_5
5.80	1.95_1	1.07	1.56	0.49	1.25_6	7.29_4
5.90	1.93_6	1.10	1.63	0.53	1.36_0	7.10_6
6.00	1.91_6	1.14	1.70	0.56	1.46_2	6.91_9
6.10	1.89_6	1.18	1.75	0.57	1.50_4	6.73_1

Table II 2.7a

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.05	2.00_0	0.83	0.93	0.10	0.25_0	10.03_9
4.10	2.00_0	0.83	0.95	0.12	0.30_1	9.94_2
4.15	2.00_0	0.84	0.98	0.14	0.35_1	9.84_5
4.20	2.00_0	0.84	1.01	0.17	0.42_6	9.74_8
4.25	2.00_0	0.84	1.03	0.19	0.47_6	9.65_1
4.30	2.00_0	0.84	1.05	0.21	0.52_6	9.55_4
4.35	2.00_0	0.84	1.07	0.23	0.57_7	9.45_7
5.20	1.99_2	0.96	1.43	0.47	1.18_1	7.80_7
5.25	1.98_2	0.98	1.47	0.49	1.23_7	7.71_2
5.30	1.97_7	0.99	1.50	0.51	1.29_1	7.61_8
5.35	1.96_7	1.01	1.55	0.54	1.37_4	7.52_6
5.40	1.95_7	1.03	1.59	0.56	1.43_2	7.37_2
5.45	1.94_7	1.05	1.63	0.58	1.49_1	7.34_0

Table II 2.8a

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
4.90	2.00_0	0.87	0.95	0.08	0.20_0	9.51_7
5.00	2.00_0	0.87	0.99	0.12	0.30_0	9.32_3
5.10	2.00_0	0.88	1.03	0.15	0.37_6	9.12_7
5.15	2.00_0	0.88	1.06	0.18	0.44_9	9.03_1
5.20	2.00_0	0.89	1.08	0.19	0.47_6	8.93_3
5.25	2.00_0	0.89	1.10	0.21	0.52_4	8.93_5
5.30	2.00_0	0.90	1.12	0.22	0.55_1	8.73_8
6.70	1.77_0	1.43	1.84	0.41	1.15_9	6.07_6
6.80	1.73_5	1.51	1.94	0.43	1.23_9	5.90_5
6.90	1.69_0	1.60	2.04	0.44	1.30_2	5.73_7
7.00	1.64_5	1.69	2.16	0.47	1.42_9	5.57_8

Fig.II 9 Cu(II)ethylenediamine system - 30°C.

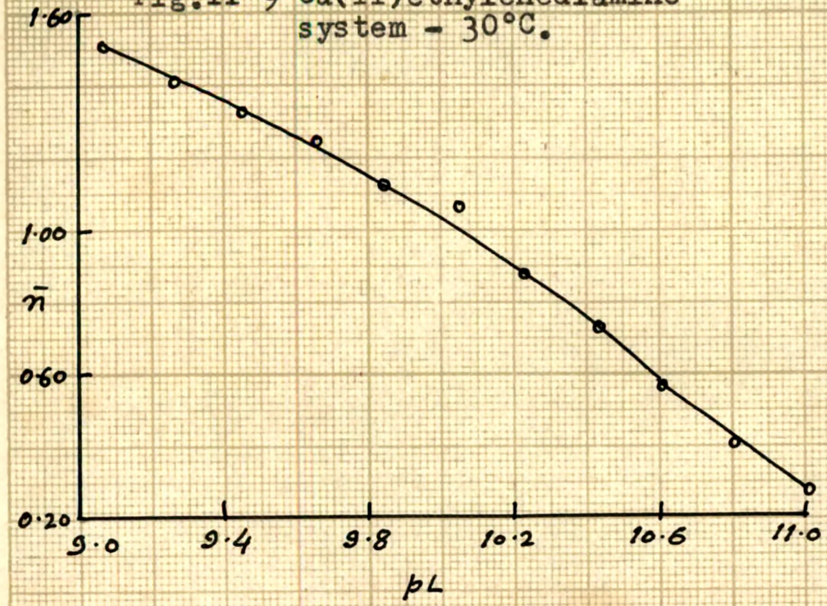


Fig.II 10 Cu(II) propylenediamine system - 30°C.

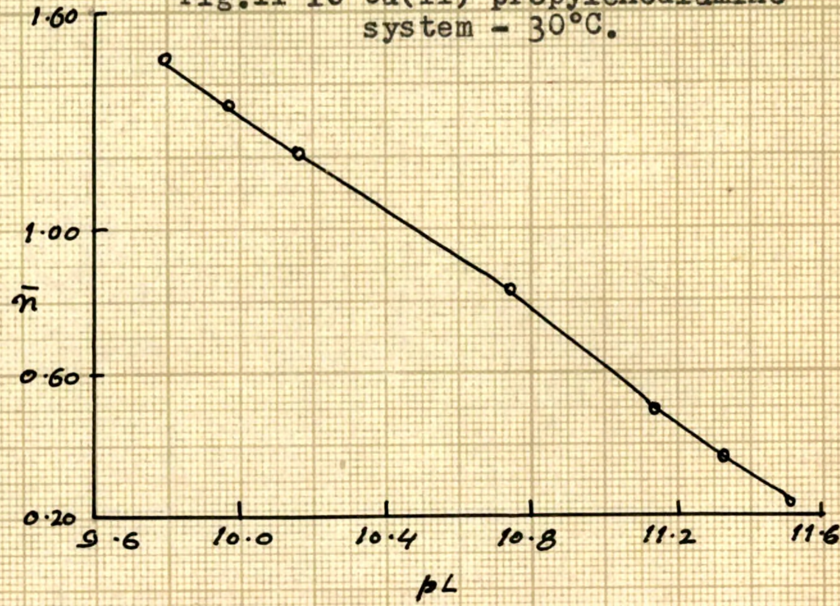


Fig.II 11(a) Cu(II) 1,3-diaminopropane system-30°C.

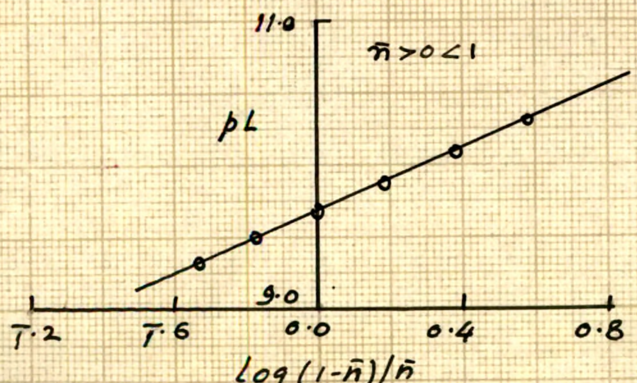


Fig.II 11(b) Cu(II) 1,3-diaminopropane system-30°C.

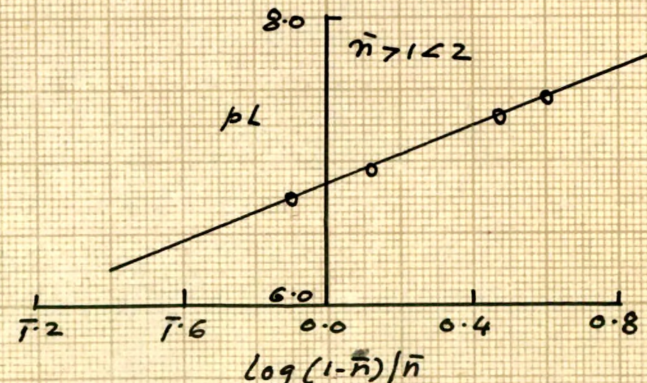


Fig.II 12 Cu(II) N-methyl en system - 30°C.

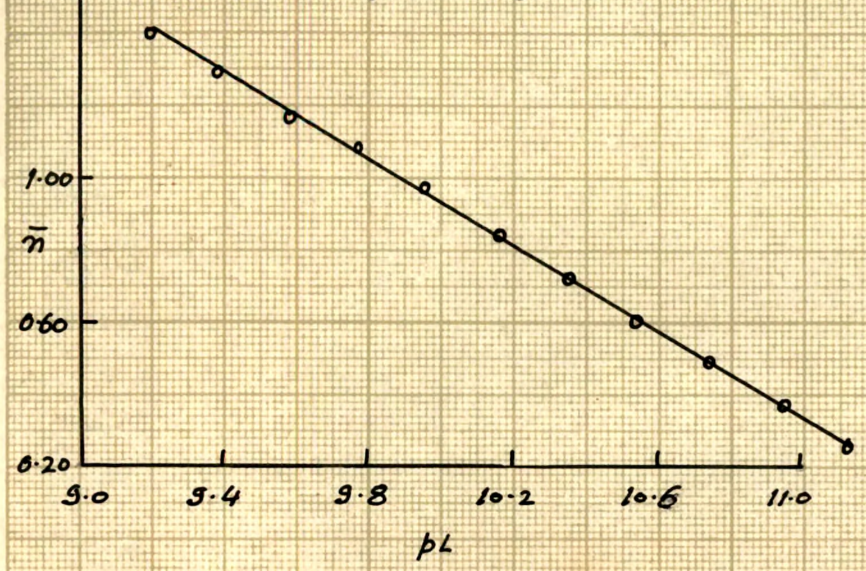


Fig.II 13 Cu(II) N-ethyl en system - 30°C.

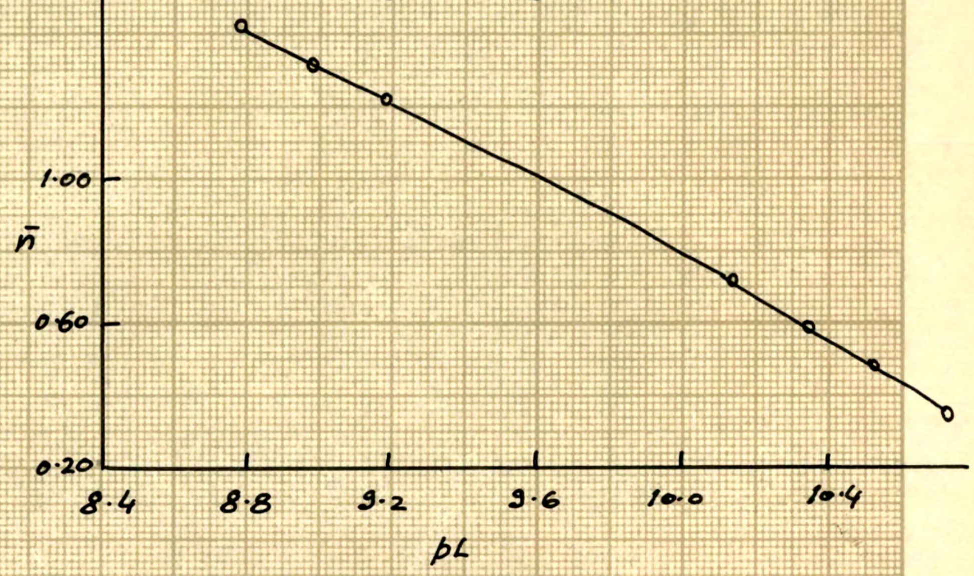


Fig.II 14(a) Cu(II) N-N'-dimethyl en system - 30°C.

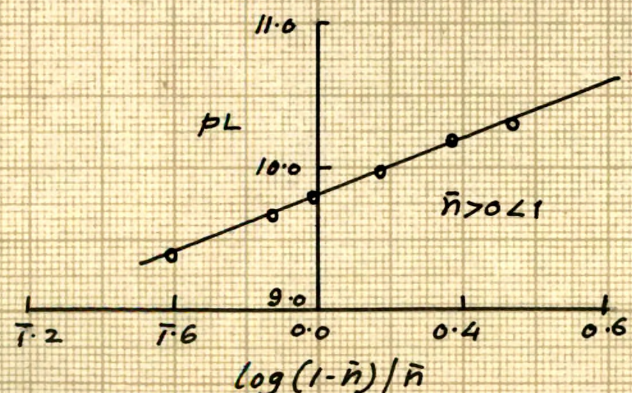


Fig.II 14(b) Cu(II) N-N'-dimethyl en system - 30°C.

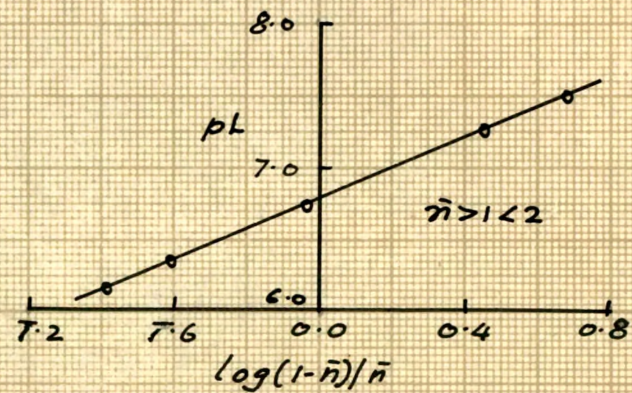


Fig. II 15(a) Cu(II) N-N-dimethyl en system - 30°C.

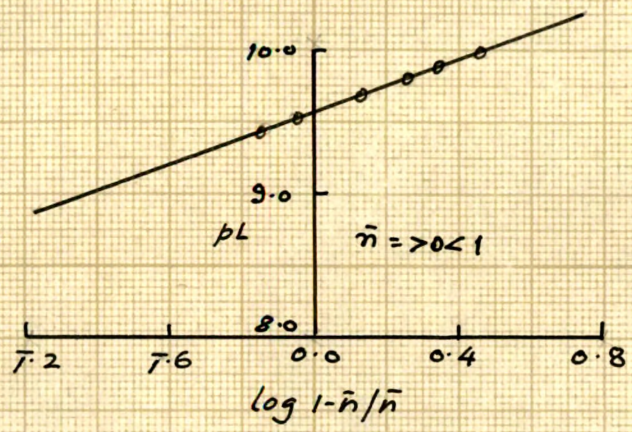


Fig.II 15(b) Cu(II) N-N-dimethyl en system - 30°C.

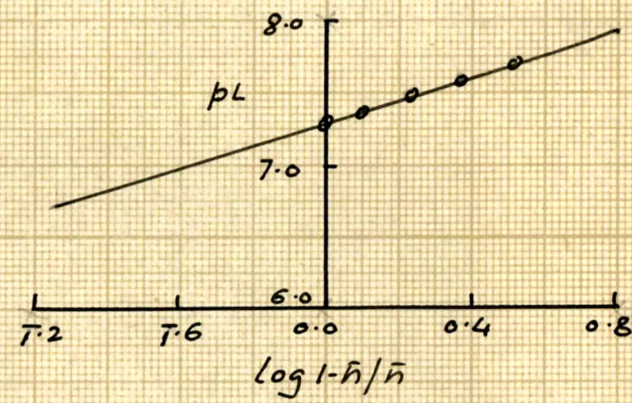


Fig. II 16(a) Cu(II) N-N-diethyl en system - 30°C.

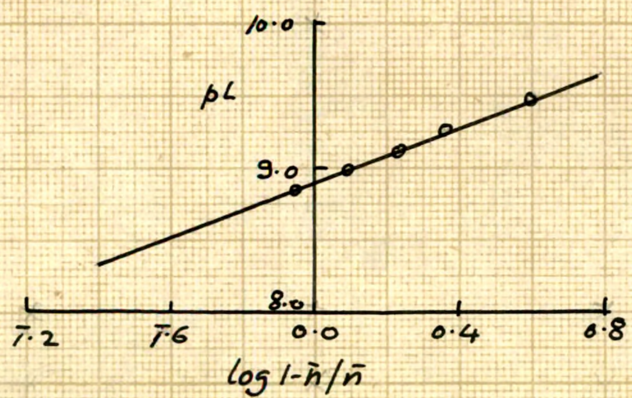


Fig.II 16(b) Cu(II) N-N-diethyl en system - 30°C.

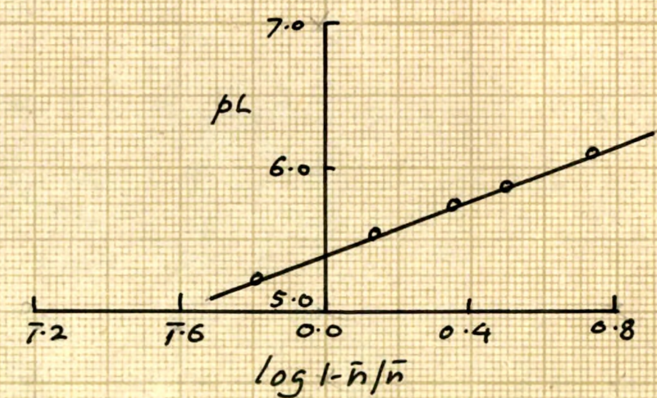


Table II 2.1b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.50	2.00_0	0.91	1.06	0.15	0.37_5	7.83_8
5.55	2.00_0	0.92	1.10	0.18	0.45_1	7.74_3
5.60	2.00_0	0.93	1.13	0.20	0.50_1	7.64_8
5.65	2.00_0	0.93	1.15	0.22	0.55_0	7.55_2
5.70	2.00_0	0.95	1.19	0.24	0.60_0	7.45_7
5.75	1.99_7	0.96	1.22	0.26	0.65_1	7.55_2
5.80	1.99_2	0.98	1.27	0.29	0.72_9	7.26_9
5.85	1.98_7	0.98	1.30	0.32	0.80_6	7.17_6
6.20	1.90_6	1.15	1.58	0.43	1.12_9	6.52_8
6.30	1.88_1	1.21	1.68	0.47	1.25_0	6.35_0
6.40	1.84_1	1.28	1.77	0.49	1.33_2	6.17_3
6.50	1.79_1	1.40	1.90	0.50	1.39_6	6.00_0

Table II 2.2b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.20	2.00_0	0.88	0.99	0.11	0.27_5	8.53_0
5.30	2.00_0	0.90	1.05	0.15	0.37_5	8.33_8
5.40	2.00_0	0.92	1.11	0.19	0.47_5	8.14_6
5.50	2.00_0	0.94	1.19	0.25	0.62_5	7.95_8
5.60	1.99_2	0.96	1.28	0.32	0.80_4	7.77_3
5.70	1.97_7	0.99	1.39	0.40	1.01_2	7.59_0
5.80	1.95_2	1.04	1.48	0.44	1.12_8	7.40_5
5.90	1.93_1	1.09	1.59	0.50	1.29_5	7.22_4
6.00	1.91_1	1.13	1.67	0.54	1.41_3	7.04_3
6.10	1.88_1	1.20	1.77	0.57	1.51_6	6.86_4

Table II 2.3b

$\bar{n}_H$, $\bar{n}$, pL data for Ni(II) 1,3-diaminopropane system - 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
7.10	2.00_0	0.91	1.02	0.11	0.27_5	6.92_8
7.20	2.00_0	0.92	1.07	0.15	0.37_5	6.73_5
7.30	2.00_0	0.93	1.11	0.18	0.45_0	6.45_1
7.40	2.00_0	0.94	1.17	0.23	0.57_5	6.35_1
7.45	2.00_0	0.95	1.20	0.25	0.62_5	6.25_1
7.50	2.00_0	0.96	1.23	0.27	0.67_5	6.16_1
7.55	2.00_0	0.98	1.27	0.29	0.72_5	6.06_0
7.60	2.00_0	0.99	1.30	0.31	0.77_5	5.97_1
7.70	1.99_0	1.02	1.36	0.34	0.85_4	5.78_2
7.80	1.97_0	1.06	1.43	0.37	0.93_9	5.61_5
8.20	1.85_0	1.30	1.76	0.46	1.24_3	4.86_9
8.30	1.80_5	1.39	1.86	0.47	1.30_2	4.69_4
8.40	1.75_0	1.50	1.97	0.47	1.34_3	4.52_4
8.50	1.70_0	1.60	2.09	0.49	1.44_1	4.36_1

Table II 2.4b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.50	2.00_0	0.92	1.03	0.11	0.27_5	8.13_0
5.60	2.00_0	0.94	1.08	0.14	0.35_0	7.93_7
5.70	2.00_0	0.96	1.13	0.17	0.42_5	7.74_4
5.80	1.99_5	0.99	1.19	0.20	0.50_1	7.55_2
5.90	1.98_0	1.02	1.27	0.25	0.63_1	7.36_5
6.00	1.96_0	1.06	1.36	0.30	0.76_5	7.17_8
6.10	1.94_0	1.10	1.44	0.34	0.87_6	6.99_2
6.20	1.91_0	1.15	1.55	0.40	1.04_7	6.81_2
6.40	1.84_5	1.29	1.73	0.44	1.19_2	6.44_8
6.50	1.81_0	1.37	1.81	0.44	1.21_5	6.26_8
6.60	1.76_5	1.46	1.94	0.48	1.36_0	6.09_8
6.70	1.72_0	1.55	2.04	0.49	1.42_4	5.92_8
6.75	1.70_0	1.60	2.10	0.50	1.47_0	5.84_6

Table II 2.5b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.80	2.00_0	0.95	1.05	0.10	0.25_0	8.13_4
5.90	2.00_0	0.98	1.11	0.13	0.32_5	7.94_1
6.00	1.98_5	1.01	1.16	0.15	0.37_8	7.75_0
6.10	1.96_5	1.05	1.25	0.20	0.50_9	7.57_7
6.20	1.94_0	1.10	1.33	0.23	0.59_3	7.37_4
6.30	1.91_5	1.16	1.43	0.29	0.75_7	7.19_0
6.40	1.88_0	1.22	1.54	0.32	0.85_1	7.00_8
6.50	1.84_5	1.29	1.67	0.38	1.03_0	6.83_1
6.60	1.81_0	1.37	1.77	0.40	1.10_5	6.65_2
6.90	1.70_0	1.60	2.02	0.42	1.26_0	6.13_5
7.00	1.64_5	1.71	2.15	0.44	1.33_7	5.97_3
7.10	1.60_0	1.80	2.27	0.47	1.46_8	5.82_0
7.20	1.54_0	1.93	2.40	0.47	1.52_5	5.66_9

Table II 2.6b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
5.60	1.97_1	1.03	1.11	0.08	0.20_3	7.63_2
5.70	1.96_1	1.04	1.16	0.12	0.30_6	7.44_1
5.80	1.95_1	1.07	1.21	0.14	0.35_9	7.24_9
5.85	1.94_1	1.09	1.25	0.16	0.41_2	7.15_4
5.90	1.93_6	1.11	1.29	0.18	0.46_5	7.06_9
6.00	1.91_6	1.14	1.34	0.20	0.52_2	6.87_0
6.05	1.90_6	1.16	1.38	0.22	0.57_7	6.71_8
7.70	1.20_0	2.61	2.91	0.30	1.25_0	4.21_9
7.80	1.17_0	2.67	2.98	0.31	1.32_4	4.10_6
7.90	1.14_0	2.72	3.04	0.32	1.40_3	3.99_7
8.00	1.11_0	2.79	3.12	0.33	1.48_6	3.89_1
8.10	1.08_5	2.83	3.17	0.34	1.56_7	3.78_6

Table II 2.7b

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

B	$\bar{n}_H$	VV"	V"'	V"'-V"	$\bar{n}$	pL
5.50	1.93_7	1.07	1.17	0.10	0.25_8	7.18_1
5.60	1.91_2	1.12	1.24	0.12	0.31_4	6.99_5
5.70	1.87_2	1.20	1.35	0.15	0.40_1	6.81_2
5.80	1.83_7	1.27	1.45	0.18	0.49_0	6.63_2
5.90	1.80_1	1.35	1.56	0.21	0.58_3	6.45_5
7.20	1.21_5	2.56	2.87	0.31	1.27_5	4.58_1
7.30	1.19_5	2.61	2.92	0.31	1.29_7	4.46_8
7.40	1.17_0	2.65	2.97	0.32	1.36_7	4.35_9
7.50	1.14_5	2.70	3.03	0.33	1.44_1	4.25_3
7.60	1.12_5	2.75	3.09	0.34	1.51_1	4.14_9
7.70	1.11_0	2.78	3.13	0.35	1.57_6	4.04_6

Table II 2.8b

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

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	pL
6.50	1.85_1	1.27	1.37	0.10	0.27_0	6.39_4
6.60	1.81_1	1.35	1.48	0.13	0.35_9	6.21_5
6.70	1.77_0	1.44	1.60	0.16	0.45_2	6.04_1
6.80	1.73_5	1.52	1.72	0.20	0.57_6	5.87_1
6.90	1.69_0	1.60	1.83	0.23	0.68_1	5.70_6
7.00	1.64_5	1.69	1.95	0.26	0.79_0	5.54_5

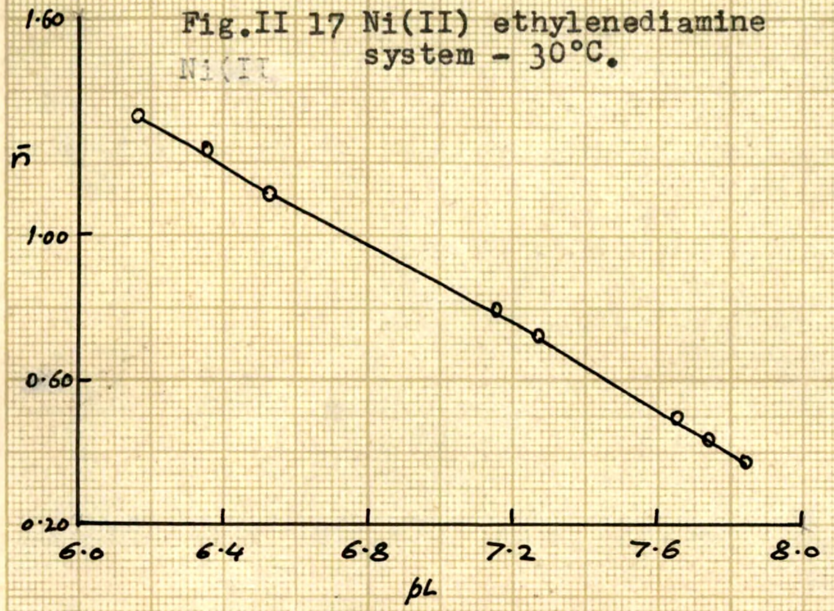


Fig.II 17 Ni(II) ethylenediamine system - 30°C.

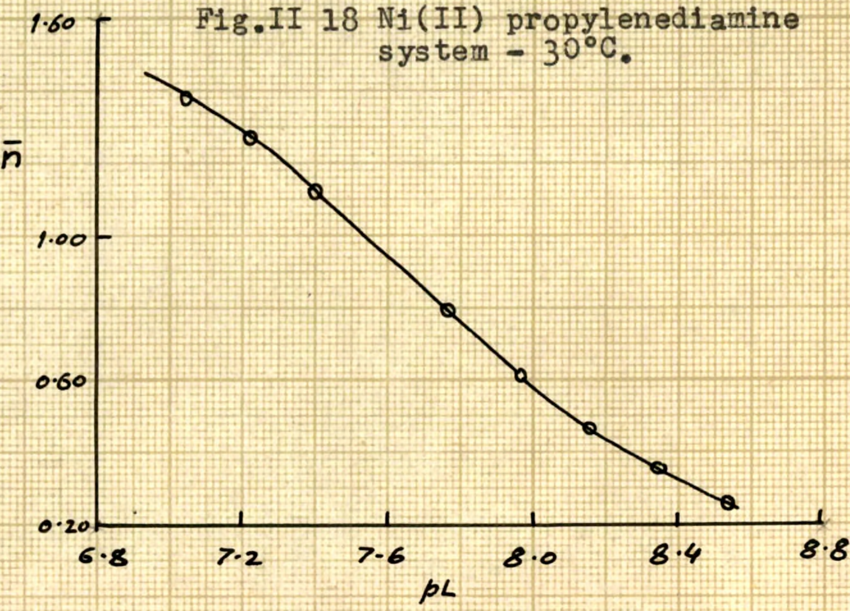


Fig.II 18 Ni(II) propylenediamine system - 30°C.

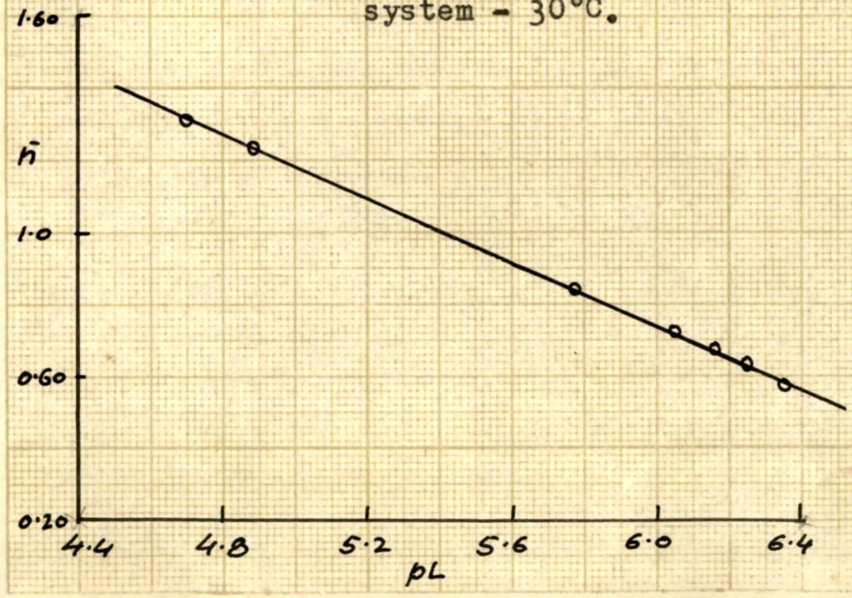


Fig.II 19 Ni(II) 1,3-diaminopropane system - 30°C.

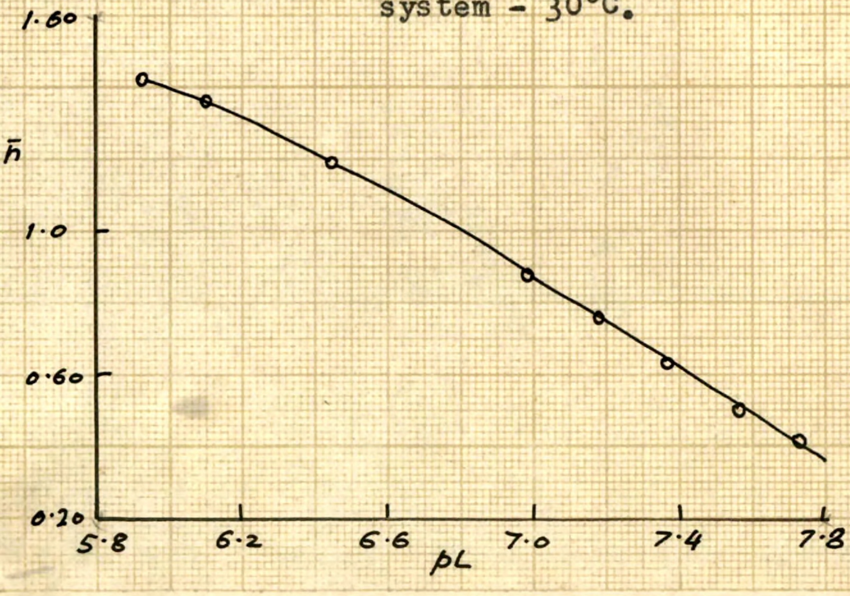


Fig.II 20 Ni(II) N-methyl en system - 30°C.

Fig. II 21 Ni(II) N-ethyl en system-30°C.

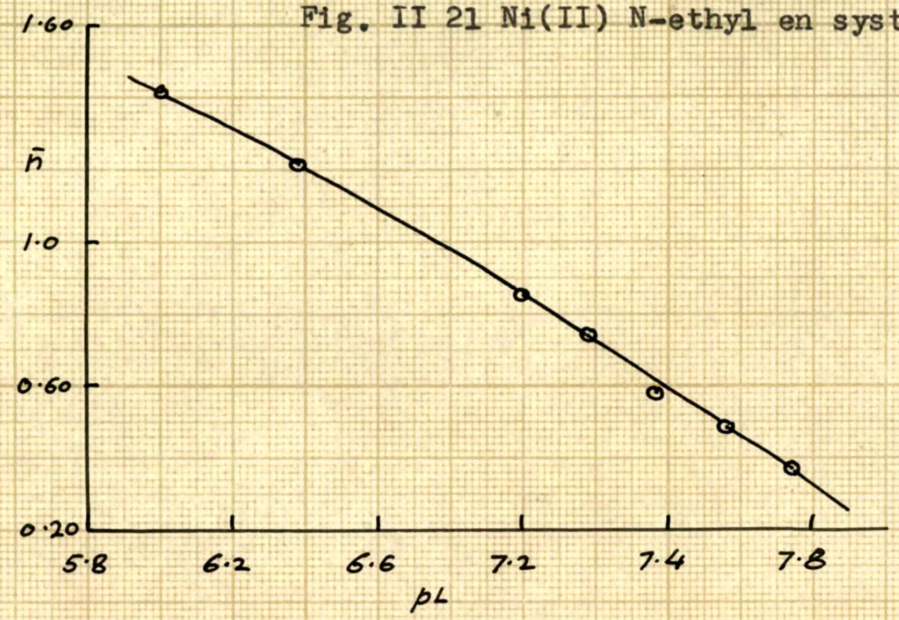


Fig. II 22(a) Ni(II) N-N'-dimethyl en system - 30°C.

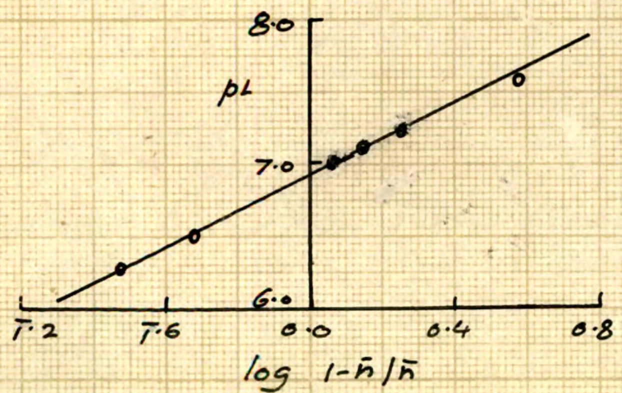


Fig.II 22(b) Ni(II) N-N'-dimethyl en system - 30°C.

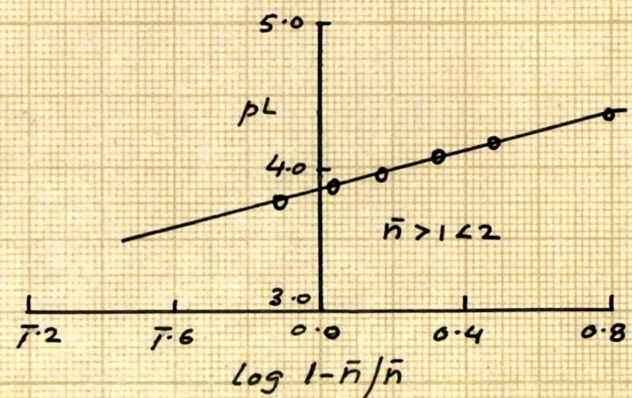


Fig.II 23(a) Ni(II) N-N-dimethyl en system - 30°C.

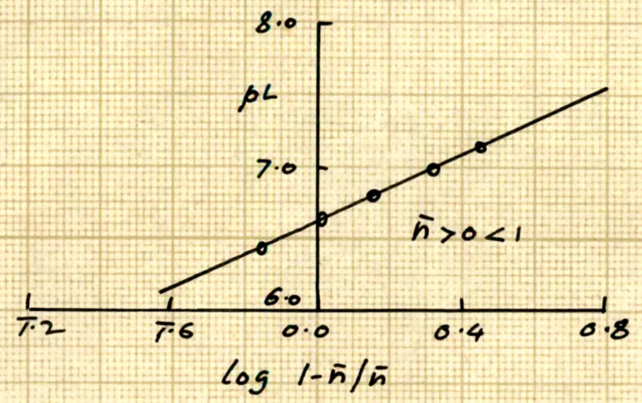


Fig.II 23(b) Ni(II) N-N-dimethyl en system - 30°C.

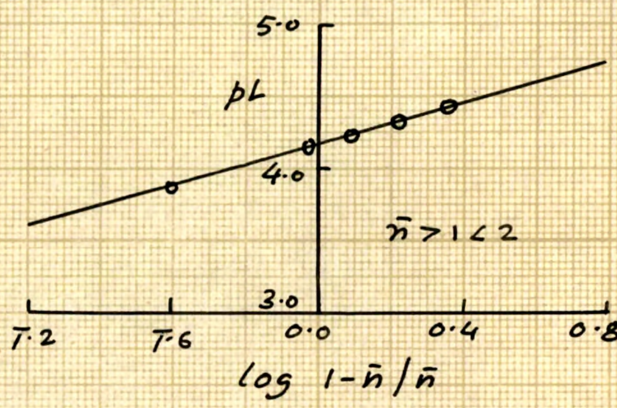


Fig.II 24 Ni(II) N-N-diethyl en system - 30°C.

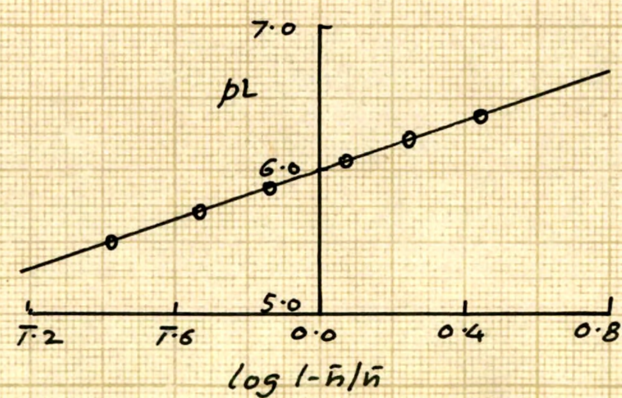


Table II 3.1a

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

$\bar{n}$	pL	y x 10^{10}	X x 10^{-10}	log β_2	log K_1	log K_2
0.57	10.63	-5.6552	-0.7795	19.91	10.70	9.21
0.70	10.44	-6.4261	-1.5734	19.95	10.71	9.24
1.35	9.47	1.1384	6.2920	19.99	10.61	9.28
1.45	9.28	0.6337	6.9566	19.91	10.71	9.20
1.53	9.08	0.3470	7.3763	19.86	10.76	9.20

log β_2=19.92$\pm$0.04
log K_1=10.70$\pm$0.03
log K_2= 9.22$\pm$0.03

Table II 3.2a

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

$\bar{n}$	pL	y x 10^{10}	x x 10^{-10}	log β_2	log K_1	log K_2
0.67	10.94	-17.6855	-0.4627	20.85	11.12	9.73
0.83	10.74	-26.8261	-1.2526	20.99	11.17	9.82
1.23	10.17	7.9098	2.2634	20.99	11.12	9.87
1.35	9.97	3.5981	1.9908	20.95	11.18	9.77
1.48	9.78	1.8574	1.7983	20.95	11.17	9.78

log β_2=20.95$\pm$0.04
log K_1=11.15$\pm$0.03
log K_2= 9.79$\pm$0.04

Table II 3.3a

$\bar{n}$, pL, log$(1-\bar{n})/\bar{n}$ and pL-log$(1-\bar{n})/\bar{n}$ data for Cu(II)1,3-diaminopropane system - 30°C.

$\bar{n}$	pL	log$(1-\bar{n})/\bar{n}$	pL-log$(1-\bar{n})/\bar{n}$
0.20_1	10.31_5	0.59_9	9.71_6
0.30_0	10.12_0	0.36_8	9.75_2
0.40_1	9.92_5	0.17_4	9.75_1
0.50_1	9.73_0	$\bar{1}.99_8$	9.73_2
0.60_2	9.53_5	$\bar{1}.81_8$	9.71_7
0.67_7	9.33_9	$\bar{1}.67_8$	9.66_1
1.12_8	7.76_5	0.83_3	6.93_2
1.20_3	7.57_0	0.59_4	6.97_6
1.25_3	7.37_4	0.47_0	6.90_4
1.32_8	7.18_0	0.31_1	6.86_9
1.42_8	6.98_7	0.12_6	6.86_1
1.55_2	6.79_6	$\bar{1}.91_3$	6.88_3

$\log K_1 = 9.72 + 0.03$
$\log K_2 = 6.90 \pm 0.03$

Table II 3.4a

$\bar{n}$, pL, y, x, logβ_2, log K_1 and log K_2 data for Cu(II)N-methylethylenediamine system - 30°C.

$\bar{n}$	pL	y x 10^{10}	x x 10^{-10}	log β_2	log K_1	log K_2
0.37	10.92	-4.8860	-0.3110	19.65	10.67	8.98
0.72	10.34	-5.6250	-2.0896	19.62	10.65	8.97
0.85	10.15	-8.0049	-5.4272	19.78	10.71	9.07
1.15	9.56	2.7838	15.6060	19.68	10.73	8.95
1.30	9.37	1.0158	9.9540	19.76	10.62	9.14
1.40	9.18	0.5297	9.9105	19.72	10.66	9.06
1.53	8.98	0.2757	9.2847	19.73	10.66	9.07

$\log B_2 = 19.70 \pm 0.05$
$\log K_1 = 10.67 \pm 0.03$
$\log K_2 = 9.07 \pm 0.05$

Table II 3.5a

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

$\bar{n}$	pL	y x 10^{10}	x x 10^{-10}	log β_2	log K_1	log K_2
0.47	10.53	-3.0050	-0.8519	19.31	10.46	8.85
0.60	10.33	-3.2072	-1.6369	19.36	10.48	8.88
0.72	10.14	-3.5497	-3.3115	19.33	10.50	8.83
1.23	9.17	0.7910	22.6346	19.20	10.28	8.92
1.33	8.98	0.3849	21.2572	19.18	10.33	8.85
1.43	8.78	0.2003	22.0046	19.14	10.38	8.76
1.48	8.59	0.1199	27.8416	19.02	10.50	8.52

log β_2=19.22$\pm$0.09
log K_1=10.42$\pm$0.08
log K_2= 8.80$\pm$0.09

Table II 3.6a

$\bar{n}$, pL, log(1-$\bar{n}$)/$\bar{n}$ and pL-log(1-$\bar{n}$)/$\bar{n}$ data for Cu(II)N-N'-dimethyl-ethylenediamine system - 30°C.

$\bar{n}$	pL	log(1-$\bar{n}$)/$\bar{n}$	pL-log(1-$\bar{n}$)/$\bar{n}$
0.17_5	10.41_5	0.67_3	9.74_2
0.22_5	10.31_8	0.53_7	9.78_1
0.30_1	10.22_2	0.36_6	9.85_6
0.40_1	10.02_6	0.17_4	9.85_2
0.50_1	9.83_2	$\bar{1}.99_8$	9.83_4
0.57_6	9.63_6	$\bar{1}.86_7$	9.76_9
1.17_3	7.48_5	0.67_9	6.80_6
1.25_6	7.29_4	0.46_3	6.83_1
1.36_9	7.10_6	0.23_3	6.87_3
1.46_2	6.91_9	0.06_6	6.85_3
1.50_4	6.73_1	$\bar{1}.99_3$	6.73_8

log K_1 = 9.80$\pm$0.04
log K_2 = 6.81$\pm$0.04

Table II 3.7a

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

$\bar{n}$	pL	$\log(1-\bar{n})/\bar{n}$	pL-$\log(1-\bar{n})/\bar{n}$
0.25_0	10.03_9	0.47_5	9.56_4
0.30_1	9.94_2	0.36_5	9.57_7
0.42_6	9.74_8	0.12_9	9.61_9
0.52_6	9.55_4	$\bar{1}.95_5$	9.59_9
0.57_7	9.45_7	$\bar{1}.86_5$	9.59_2
1.18_1	7.80_7	0.65_8	7.14_9
1.29_1	7.61_8	0.38_9	7.22_9
1.37_4	7.52_6	0.23_1	7.29_5
1.43_2	7.37_2	0.12_2	7.25_0
1.49_1	7.34_0	0.01_7	7.32_3

$\log K_1 = 9.59 \pm 0.02$
$\log K_2 = 7.24 \pm 0.05$

Table II 3.8a

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

$\bar{n}$	pL	$\log(1-\bar{n})/\bar{n}$	pL-$\log(1-\bar{n})/\bar{n}$
0.20_0	9.51_7	0.60_2	8.91_5
0.30_0	9.32_3	0.36_8	8.95_5
0.37_6	9.12_7	0.22_0	8.90_7
0.44_9	9.03_1	0.08_9	8.94_2
0.47_6	8.93_3	0.04_2	8.89_1
0.52_4	8.93_5	$\bar{1}.95_8$	8.97_7
0.55_1	8.73_8	$\bar{1}.91_1$	8.82_7
1.15_9	6.07_6	0.72_0	5.35_6
1.23_9	5.90_5	0.50_1	5.40_4
1.30_2	5.73_7	0.36_4	5.37_3
1.42_9	5.57_8	0.12_2	5.45_6

$\log K_1 = 8.91 \pm 0.03$
$\log K_2 = 5.39 \pm 0.03$

Table II 3.1b

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

$\bar{n}$	pL	y x 10^7	x x 10^{-7}	log β_2	log K_1	log K_2
0.55	7.55	-4.3372	-0.9080	13.55	7.60	5.95
0.73	7.27	-5.0348	-2.5259	13.53	7.61	5.92
0.80	7.17	-5.9163	-4.0566	13.63	7.64	5.99
1.13	6.53	2.9455	19.7490	13.55	7.63	5.92
1.25	6.35	1.1193	13.4010	13.59	7.58	6.01
1.33	6.17	0.5961	13.7268	13.54	7.64	5.90

log β_2=13.56$\pm$ 0.03
log K_1= 7.61$\pm$ 0.02
log K_2= 5.95$\pm$ 0.03

Table II 3.2b

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

$\bar{n}$	pL	y x 10^7	x x 10^{-7}	log β_2	log K_1	log K_2
0.37	8.34	-12.8484	-0.1182	15.15	8.08	7.11
0.62	7.96	-14.8866	-0.3980	14.99	8.00	6.99
0.80	7.77	-23.5571	-1.0188	15.09	8.04	7.05
1.13	7.40	21.8345	2.6642	15.09	8.02	7.07
1.29	7.22	7.3818	1.4753	15.09	8.02	7.07
1.41	7.04	3.7708	1.3124	15.05	8.08	6.97

log β_2=15.08$\pm$0.05
log K_1= 8.04$\pm$0.03
log K_2= 7.04$\pm$0.03

Table II 3.3b

$\bar{n}$, pL, Y, x, log β_2, log K_1 and log K_2 data for Ni(II) 1,3,diamino-propane system - 30°C.

$\bar{n}$	pL	$y \times 10^5$	$x \times 10^{-5}$	log β_2	log K_1	log K_2
0.62	6.25	-29.0161	-0.2042	10.82	6.44	4.38
0.67	6.16	-29.3481	-0.2788	10.78	6.44	4.34
0.72	6.06	-29.5227	-0.3981	10.67	6.44	4.23
0.77	5.97	-31.2297	-0.5733	10.79	6.45	4.34
1.30	4.69	2.1221	4.7646	10.79	6.37	4.42
1.34	4.52	1.3050	5.8623	10.69	6.47	4.22
1.44	4.36	0.7097	5.5554	10.70	6.46	4.24

log β_2=10.75$\pm$0.05
log K_1= 6.44$\pm$0.02
log K_2= 4.31$\pm$0.07

Table II 3.4b

$\bar{n}$, pL, y, x, log β_2, log K_1 and log k_2 data for Ni(II)N-methyl-ethylenediamine system - 30°C.

$\bar{n}$	pL	$y \times 10^6$	$x \times 10^{-6}$	log β_2	log K_1	log K_2
0.76	7.18	-47.9289	-0.3413	13.37	7.59	5.78
0.87	6.99	-65.4184	-0.8892	13.46	7.62	5.84
1.21	6.26	-10.4857	2.0671	13.38	7.64	5.74
1.36	6.10	4.7561	1.4121	13.50	7.51	5.99
1.42	5.93	2.8774	1.6226	13.42	7.60	5.82
1.47	5.84	2.1644	1.6294	13.41	7.61	5.80

log β_2=13.42$\pm$0.03
log K_1= 7.59$\pm$0.03
log K_2= 5.83$\pm$0.06

Table II 3.5b

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

$\bar{n}$	pL	$y \times 10^6$	$X \times 10^{-6}$	log β_2	log K_1	log K_2
0.51	7.56	-37.7929	-0.0837	13.22	7.56	5.67
0.75	7.19	-46.4612	-0.3228	13.43	7.60	5.83
1.26	6.13	6.5373	2.1098	13.32	7.56	5.76
1.33	5.97	3.7596	2.1765	13.28	7.60	5.68
1.47	5.82	2.0658	1.7072	13.36	7.51	5.85
1.52	5.66	1.3359	2.0197	13.28	7.60	5.68

log β_2=13.31±0.04
log K_1= 7.57±0.03
log K_2= 5.74±0.07

Table II 3.6b

$\bar{n}$, pL, log(1-$\bar{n}$)/$\bar{n}$ and pL - log(1-$\bar{n}$)/$\bar{n}$ data for Ni(II)N-N'-dimethyl-ethylenediamine system - 30°C.

$\bar{n}$	pL	log(1-$\bar{n}$)/$\bar{n}$)	pL-log(1-$\bar{n}$)/$\bar{n}$
0.20_3	7.63_2	0.59_4	7.03_8
0.30_6	7.44_1	0.35_5	7.08_6
0.35_9	7.24_9	0.25_2	6.99_7
0.41_2	7.15_4	0.15_4	7.00_0
0.46_5	7.06_9	0.06_1	7.00_8
0.52_2	6.87_0	$\bar{1}.96_1$	6.90_9
0.57_7	6.77_8	$\bar{1}.86_5$	6.91_3
1.25_0	4.21_9	0.47_7	3.74_2
1.32_4	4.10_6	0.32_7	3.77_9
1.40_3	3.99_7	0.17_0	3.82_7
1.48_6	3.89_1	0.02_4	3.86_7
1.56_7	3.78_6	$\bar{1}.88_3$	3.90_3

log K_1 = 6.99±0.05
log K_2 = 3.82±0.05

Table II 3.7b

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

$\bar{n}$	pL	$\log(1-\bar{n})/\bar{n}$	pL$-\log(1-\bar{n})/\bar{n}$
0.25_8	7.18_1	0.45_9	6.72_2
0.31_4	6.99_5	0.33_9	6.65_6
0.40_1	6.81_2	0.17_4	6.63_8
0.49_0	6.63_2	0.01_7	6.61_5
0.58_3	6.45_5	$\bar{1}.85_4$	6.60_1
1.27_5	4.58_1	0.42_1	4.16_0
1.29_7	4.46_8	0.37_4	4.09_4
1.36_7	4.35_9	0.23_6	4.12_3
1.44_1	4.25_3	0.10_4	4.14_9
1.51_1	4.14_9	$\bar{1}.98_1$	4.16_8
1.57_6	4.04_6	$\bar{1}.86_7$	4.17_9

$\log K_1 = 6.64 \pm 0.03$
$\log K_2 = 4.14 \pm 0.03$

Table II 3.8b

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

$\bar{n}$	pL	$\log(1-\bar{n}/\bar{n}$	pL$-\log(1-\bar{n})/\bar{n}$
0.27_0	6.39_4	0.43_1	5.96_3
0.35_9	6.21_5	0.25_2	5.96_3
0.45_2	6.04_1	0.08_3	5.95_8
0.57_6	5.87_1	$\bar{1}.86_7$	6.00_4
0.68_1	5.70_6	$\bar{1}.67_0$	6.03_6
0.79_0	5.54_5	$\bar{1}.42_5$	6.12_0

$\log K_1 = 6.00 \pm 0.05$

Table II 4.0

Proton ligand stability constants of various diamines - 30°C.

Ligand (L)	$P_{K_2}^H$	$P_{K_1}^H$
Ethylenediamine(en)	7.00 ± (0.02)	10.10 ±(0.01)
Propylenediamine(pn)	6.80 ± (0.03)	10.40 ±(0.02)
1,3-Diaminopropane	8.80 ± (0.01)	10.60 ±(0.02)
N-Methyl en	7.10 ± (0.01)	10.30 ±(0.01)
N-Ethyl en	7.25 ± (0.02)	10.75 ±(0.01)
N-N'-Dimethyl en	7.05 ± (0.02)	10.05 ±(0.02)
N-N-Dimethyl en	6.50 ± (0.03)	9.92 ±(0.01)
N-N-Diethyl en	7.25 ± (0.01)	10.35 ±(0.01)

Table II 5.0

Formation constants of various metal ligand complexes at 30°C.

Ligand (L)		Copper(II)	Nickel(II)
Ethylenediamine(en)	$\log K_1$	10.70 ± 0.03	7.61 ± 0.02
	$\log K_2$	9.22 ± 0.03	5.95 ± 0.03
Propylenediamine(pn)	$\log K_1$	11.15 ± 0.03	8.04 ± 0.03
	$\log K_2$	9.79 ± 0.04	7.04 ± 0.03
1,3-diaminopropane	$\log K_1$	9.72 ± 0.03	6.44 ± 0.02
	$\log K_2$	6.90 ± 0.03	4.31 ± 0.07
N-Methyl en	$\log K_1$	10.67 ± 0.03	7.59 ± 0.03
	$\log K_2$	9.07 ± 0.05	5.83 ± 0.06
N-Ethyl en	$\log K_1$	10.42 ± 0.08	7.57 ± 0.03
	$\log K_2$	8.80 ± 0.09	5.74 ± 0.07
N-N'-dimethyl en	$\log K_1$	9.80 ± 0.04	6.99 ± 0.05
	$\log K_2$	6.81 ± 0.04	3.82 ± 0.05
N-N-Dimethyl en	$\log K_1$	9.59 ± 0.02	6.64 ± 0.03
	$\log K_2$	7.24 ± 0.05	4.14 ± 0.03
N-N-Diethyl en	$\log K_1$	8.91 ± 0.03	6.00 ± 0.05
	$\log K_2$	5.39 ± 0.03	-

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