CHAPTER II

BINARY METAL POLYPHENOLIC LIGAND SYSTEMS

Study of the binary systems containing Cu(II) or Ni(II) and polyphenols have been carried out earlier. Cu(II) complexes of catechol have been studied by polarographic[1,2] and potentiometric method.[3,4,5] Athavale and coworkers[6] studied Cu(II), Ni(II) complexes of catechol and protocatechuic acid using Calvin-Bjerrum titration technique. Murakami and coworkers[7] have determined formation constants of bivalent metals including Cu(II) and Ni(II) with catechol. The stability constants of Cu(II) or Ni(II) and catechol systems have also been determined by absorptiometric method.[8,9] Cu(II) complexes with protocatechuic acid have been studied by spectrophotometric method.[10] The stability constants of Cu(II) and Ni(II) complexes with protocatechuic acid have also been determined by potentiometric method.[11]

Recently Patel and Bhattacharya[12,13] have determined the formation constants of Cu(II) and Ni(II) complexes with polyphenols using Irving-Rossotti titration technique, wherein, the ligand was in excess. In the present investigation, however, in the determination of the mixed ligand formation constants K_{MAL}, as reported in later chapter, metal ion, primary and secondary ligands have been taken in 1:1:1 ratio. In order to compare K_{MAL} with K_{ML}, the latter determination should be done under identical conditions. As such the formation constants of binary systems Cu(II) or Ni(II) and ligands catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid have been determined taking metal and ligand in 1:1 ratio.

Polyphenolic complexes of large number of other metal ions have also been studied. This has been detailed in an earlier thesis.[14] However, studies with Be(II), Al(III) and Co(II) are not much.

Be(II) complexes of catechol 1:1 and 1:2 have been studied using potentiometric and conductometric methods.[15] Be(II), Sn(IV) complexes of catechol have been studied by potentiometric method.[16,17] The complex formation of pyrogallol with Al(III)[18] and Be(II)[19] have been investigated by potentiometric, conductometric and polarographic methods.

The formation constants of Co(II), Be(II) and Al(III) complexes with polyphenol have not been determined using Irving-Rossotti titration technique. This has been undertaken in the present investigation. This was considered to be of help in revealing the complexing tendency of the compounds used as secondary ligand in the later ternary systems and also to indicate the relative stability of the complexes of transition and non-transition metal ions.

(A) Experimental :

Metal ligand formation constants in solution were determined by using Irving-Rossotti titration technique. The titrations were carried out in the aqueous medium since the metal salt and ligands used are freely soluble in water. 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. The purity was checked by taking the melting points. The ligands used were catechol (E.Merck, Germany), pyrogallol (A.R.B.D.H.), 2,3-dihydroxynaphthalene (A.R., Fluka), protocatechuic acid (A.R., Fluka). Their standard solutions were prepared by dissolving the weighed quantity in known volume of double distilled water. Since the ligands have a tendency to get oxidised, fresh solutions were always prepared.

(i) Sodium hydroxide : The solution was prepared by dissolving 50 gms. sodium hydroxide (Chemapol, Czechoslovakia) 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 CO_2 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., Fluka) was weighed and dissolved in 500 ml. of double distilled water to prepare a 1M solution.

(iii) Perchloric acid solution : The perchloric acid (Baker 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 0.5M strength. The exact concentration was determined by titrating against standard sodium hydroxide.

(iv) Metal salt solution : The metal perchlorates could not be used because while preparing $Co(ClO_4)_2$ from $CoCO_3$ and $HClO_4$, Co(II) gets partly oxidised to Co(III), Beryllium and Aluminium carbonates were not available in the pure form, for the preparation of the perchlorates. In order to avoid the complexing tendencies of the anion the solutions of less complexing nitrates of metals were prepared by dissolving certain amount of metal nitrates (A.R., BDH) in double distilled water and diluting it to exact volume. The concentration of solutions were determined by estimating the amount of metal in it. From this standard stock solution 0.01M metal nitrate was prepared by proper dilution.

Copper(II) and Nickel(II) perchlorates could be prepared by dissolving excess metal carbonates (A.R., BDH) in perchloric acid solution and refluxing the mixture for two hours. It was filtered and metal contents were determined. The solution was diluted to get metal perchlorate of 0.01M strength.

(b) pH meter and accessories :

A Metrohm pH meter of type E 350A operating on 220-240 volts and 40-60 cycle 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 ± 0.05 pH unit and a reproducibility of 0.02 pH unit. It was calibrated with buffer of 4 and 7 pH. The calibration was intermittently checked.

(c) Details of the 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 the burette tip and glass stirrer. In all three sets were prepared as follows :

I For systems Cu(II) and Ni(II), the M:L ratio is 1:1

(i) 0.02M perchloric acid, 0.180M sodium perchlorate

(ii) 0.02M perchloric acid, 0.002M ligand, 0.178M sodium perchlorate.

(iii) 0.02M perchloric acid, 0.002M ligand, 0.002M metal perchlorate, 0.176M sodium perchlorate.

II For systems Co(II), Be(II) and Al(III) with excess of ligand :

(i) 0.01M perchloric acid, 0.190M sodium perchlorate.

(ii) 0.01M perchloric acid, 0.01M ligand, 0.180M sodium perchlorate.

(iii) 0.01M perchloric acid, 0.01M ligand, 0.001M metal nitrate, 0.179M sodium perchlorate.

In each case total volume was maintained 50.0 ml. by addition of double distilled water and the initial ionic strength was raised to 0.2M by the addition of neutral sodium perchlorate.

The titration beakers were allowed to stand in the thermostat in order to attain the temperature 30°C. During the titrations nitrogen gas was passed through the solution in the beaker to avoid the aerial oxidation of the ligand. After addition of each portion of alkali, pH was noted. The highest reading which remained steady was recorded in all the cases. The titration data and curves are given in tables II 1 to II 4 and in figs. II 1 to II 5, respectively. In consideration of the limited space, titration data for the whole pH region has not been presented. Only the regions, where there is substantial pH change on the addition of each 0.02 ml. of alkali, have been recorded.

Determination of proton ligand and metal ligand stability constants :

As seen in the Irving-Rossotti titration curves Figs. II 1 to II 5, 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 titrable H^+ ions due to the dissociation of -OH groups. The ligands are thus weak acids. In case of protocatechuic acid the separation between the two curves starts at lower pH because -COOH group undergoes dissociation at lower pH. From the displacement of these curves $\bar{n}_H$ can be calculated by using the following equation :

$$\bar{n}_H = \frac{(V' - V'')(N + E^\circ)}{(V^\circ + V')\, T_L^\circ} + Y \qquad (2.1)$$

The details of intermediate stages of calculations and graphs have not been given because such data have been incorporated in the thesis submitted earlier[14]. However, the calculations had to be repeated to get K^H values under experimental conditions.

The advantage of Irving-Rossotti method of determination of formation constants is that from the values of $\bar{n}_H$ calculated, proton ligand stability constants can also be determined under the experimental conditions. The accurate determination of these values are essential because the values of pL are dependent on them.

Further metal complex is formed by reaction of the type

$$M^{2+} + LH_2 \rightleftharpoons ML^{+} + 2H$$

Thus the ligand on coordination with metal releases extra H^+ ions in solution and hence the metal + ligand solution contains still more titrable hydrogen ions. The metal + ligand curve, therefore, shows lower pH value for the same amount of alkali than the ligand titration curve. Thus $\bar{n}$ factor can be calculated from the difference in volume of alkali required to produce the same pH in the metal and ligand titrations. To put in otherwords, the displacement of the metal curve has to be measured with respect to the reagent curve along the volume axis in the "pH versus volume of alkali" plot.

The $\bar{n}$ values can be calculated from the equation

$$\bar{n} = \frac{\left[(V''' - V'') \left\{N + E^\circ + T^\circ_L (Y - \bar{n}_H)\right\}\right]}{(V^\circ + V'')\, \bar{n}_H T^\circ_M} \qquad (2.2)$$

Since metal nitrates have been used and the titrations have been carried out using dilute solutions, it is presumed that species such as undissociated metal salt, polynuclear complex, hydroxy complexes are not present. The absence of hydroxy complexes or the metal hydroxide has been ascertained by using the range of the pH where there is smooth increase in the curves. At higher pH with probability of hydroxy complex formation, there is suddenly increase in the distance between ligand curve and metal + ligand curve.

The portions of the titration curve at very low pH, having small separation were avoided.

For the calculation of pL in case of catechol, pyrogallol and 2,3-dihydroxynaphthalene the equation is

$$pL=\log\left[\frac{1 + {}^{P}K_1^H\left(\frac{1}{\text{antilog } B}\right) + {}^{P}K_1^H . {}^{P}K_2^H\left(\frac{1}{\text{antilog } B}\right)^2}{T_L^o - \bar{n}.T_M^o} \cdot \frac{V^o + V'''}{V^o}\right] \qquad (2.3)$$

In case of protocatechuic acid the equation used contains one more term ${}^{P}K_1^H . {}^{P}K_2^H . {}^{P}K_3^H \left(\frac{1}{\text{antilog } B}\right)^3$

$$pL=\log\left[\frac{1 + {}^{P}K_1^H\left(\frac{1}{\text{antilog} B}\right) + {}^{P}K_1^H . {}^{P}K_2^H\left(\frac{1}{\text{antilog} B}\right)^2 + {}^{P}K_1^H . {}^{P}K_2^H . {}^{P}K_3^H\left(\frac{1}{\text{antilog} B}\right)^3}{T_L^o - \bar{n}.T_M^o} \cdot \frac{V^o + V'''}{V^o}\right]$$

pL values at different pH have been presented in tables II 6 to II 16. At $\bar{n}$ = 0.5 and 1.5 pL corresponds to log K_1 and log K_2. Since in the case of the complexes studied $K_1 / K_2 > 10^{2.5}$, the above method can be used. However, determination of formation constant from pL at one point may involve experimental error.

Since the stepwise formation constants differ significantly there will not be simultaneous formation of the species ML_1 and ML_2. The method based on the use of formation function, such as simultaneous equations and least square methods cannot, therefore, be used for the calculation of precise values.

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 6 to II 23. The value 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 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 values was calculated. The average values of $\log K_1$ and $\log K_2$ with mean deviation have been presented in table II 17.

In case of Co(II) since $\bar{n}$ does not go beyond 1, only log K_1 values were calculated. In case of Cu(II) and Ni(II) complexes also, as expected, $\bar{n}$ beyond 0.7 could not be obtained and log K_1 was calculated by using the method of averages and from linear plot. The values of K_{ML_1}, obtained in case of Cu(II) and Ni(II) by taking M : L in 1 : 1 ratio, are found to be approximately same as those obtained by Patel and Bhattacharya[12,13] using excess of ligand.

In case of Co(II), Be(II), Al(III), Cu(II) and Ni(II) complexes the order of stabilities is 2,3-dihydroxynaphthalene > protocatechuic acid > catechol > pyrogallol. This is in accordance with basicities of the ligands except in case of protocatechuic acid. Though more acidic, it forms more stable complexes than catechol. Similar observations have been made by earlier workers[7]. This can be explained by considering that the coordination in protocatechuic acid is through two -OH groups. This is shown by the fact that in case of both catechol and protocatechuic acid complexes, ligand and metal + ligand curves separate in the same pH range. If there would have been coordination from -COOH group, separation of metal + ligand and ligand curve should have started at lower pH. The coordination of -COOH group from the meta position is also less likely[20].

Since the complexation takes place in the pH range where -COOH dissociation is complete, Y is to be considered three.

In case of beryllium and aluminium complexes of protocatechuic acid, since complexation is at low pH where $\bar{n}_H$ is greater than 2, incomplete self dissociation of -COOH is indicated. Since -COOH does not coordinate, the carboxylate H will remain bound even after complex formation. In these cases Y is considered to be two for $\bar{n}$ calculations. In other words $\bar{n}$ has been calculated by using Calvin-Melchior method[21]. In pL calculation, however, three proton ligand formation constants have been considered in order to account for the extent of dissociation of -COOH group.

Since the coordination takes place from -OH group only, the proton ligand formation constants corresponding to -OH group will only affect the stability constants. $P_{K_1^H}$ and $P_{K_2^H}$ values of protocatechuic acid are higher than that of catechol and pyrogallol and hence protocatechuate complexes are naturally expected to be more stable.

The order of metal ligand stability constants are Co $<$ Ni $<$ Be $<$ Cu $<$ Al.

Aluminium and beryllium ions, though non-transition in character, have smaller ionic radii. This results in the increased in M-O bond stability. Aluminium ion with three positive charges forms more stable complexes than Be^{2+}.

Co(II) forms less stable complexes than Ni(II) and Ni(II) forms less stable complexes than Cu(II). This shows that Cu(II), Ni(II) and Co(II) are in accordance with Irving-Williams order,[22] and the stability can be explained in terms of CFSE and John-Tellor effect.[23]

Table II 1

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

$E^\circ = 0.01M$ $T^\circ_L = 0.01M$ $T^\circ_M = 0.001M$

Perchloric acid		Catechol		Al(III)		Be(II)		Co(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	1.70	0.00	1.70	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
1.50	2.20	1.50	2.20	1.50	2.20	1.50	2.20	1.50	2.20
2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70
2.10	2.80	2.10	2.80	2.10	2.80	2.10	2.80	2.10	2.80
2.20	2.95	2.20	2.95	2.20	2.95	2.20	2.95	2.20	2.95
2.30	3.10	2.30	3.10	2.30	3.05	2.30	3.10	2.30	3.10
2.40	3.55	2.40	3.55	2.40	3.15	2.40	3.55	2.40	3.55
2.44	3.75	2.44	3.75	2.50	3.30	2.44	3.75	2.44	3.75
2.48	3.90	2.48	3.90	2.58	3.40	2.50	4.04	2.50	3.90
2.50	4.05	2.50	4.05	2.64	3.55	2.52	4.60	2.52	4.05
2.52	9.05	2.52	5.10	2.74	3.70	2.54	4.75	2.54	5.70
2.54	9.25	2.53	6.25	2.80	3.90	2.58	4.95	2.56	6.25
2.56	9.40	2.54	7.20	2.84	4.00	2.60	5.00	2.58	7.00
2.58	9.60	2.56	7.30	2.90	4.20	2.68	5.25	2.60	7.10
2.60	9.70	2.60	7.50	2.94	4.30	2.78	5.50	2.64	7.20
2.64	9.90	2.64	7.75	3.00	4.50	2.84	5.75	2.68	7.35
2.66	10.05	2.68	7.95	3.06	4.75	2.88	5.95	2.72	7.45
2.68	10.15	2.72	8.10	3.10	4.95	2.96	6.25	2.76	7.55
2.70	10.25	2.76	8.20	3.18	5.20	3.00	6.50	2.80	7.65
2.74	10.40	2.80	8.30	3.20	5.30	3.04	6.75	2.84	7.75
2.78	10.50	2.86	8.40	3.24	5.40	3.08	7.00	2.90	7.85

Table II 1 (contd.)

2.80	10.60	2.94	8.50	3.30	5.50	3.16	7.20	3.00	8.00
2.84	10.70	3.04	8.60	3.38	5.70	3.24	7.50		(ppt.)
2.88	10.80	3.20	8.80	3.44	5.90	3.28	7.60		
2.90	10.90	3.30	8.90	3.50	6.05	3.40	7.75		
2.94	11.00	3.40	9.00	3.54	6.20	3.50	7.90		
		3.50	9.10	3.58	6.40	3.60	8.05		
		3.70	9.25	3.60	6.50	3.70	8.25		
		3.80	9.30	3.64	6.60	3.80	8.40		
		3.90	9.40	3.70	6.90	3.90	8.60		
		4.20	9.50	3.78	7.15	4.00	8.75		
		4.40	9.60	3.84	7.40	4.08	8.90		
		4.70	9.75	3.90	7.70	4.20	9.05		
		4.80	9.80	3.98	7.95	4.40	9.20		
		5.00	10.00	4.06	8.10	4.50	9.35		
		5.20	10.25	4.10	8.20	4.60	9.40		
		5.30	10.40	4.20	8.35	4.70	9.45		
		5.50	10.70	4.28	8.50	4.80	9.55		
		5.60	10.80	4.40	8.65	4.90	9.65		
		5.70	11.00	4.50	8.80		(ppt.)		
				4.60	8.90				
				4.70	9.05				
				4.80	9.15				
				5.00	9.30				
					(ppt.)				

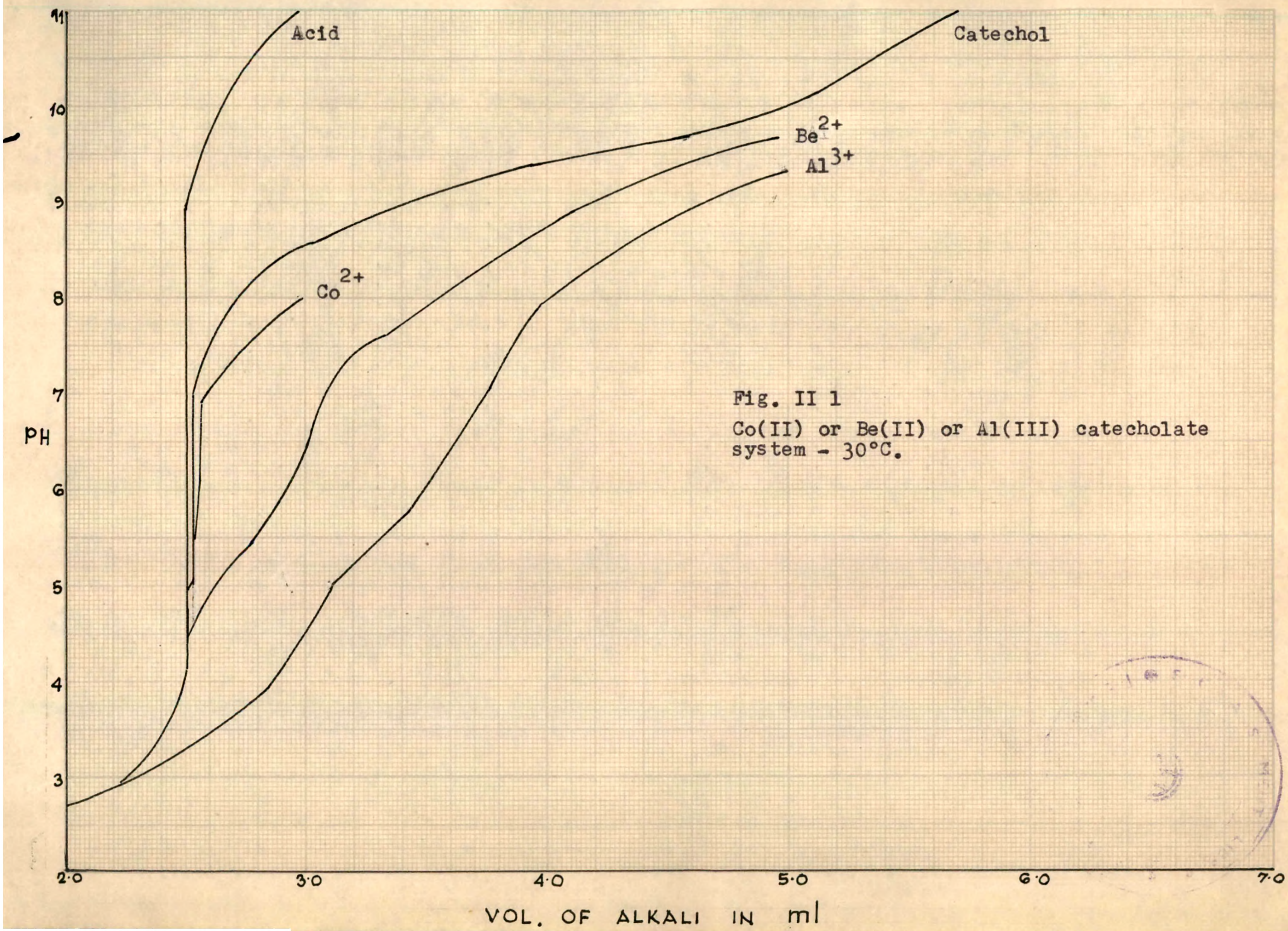


Fig. II 1

Co(II) or Be(II) or Al(III) catecholate system - 30°C.

Table II 2

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

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

Perchloric acid		Pyrogallol		Al(III)		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	1.70	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
1.50	2.20	1.50	2.20	1.50	2.20	1.50	2.20
2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70
2.10	2.90	2.10	2.90	2.10	2.90	2.10	2.90
2.20	3.05	2.20	3.05	2.20	3.05	2.20	3.05
2.30	3.20	2.30	3.25	2.30	3.10	2.30	3.20
2.35	3.30	2.40	3.50	2.36	3.20	2.35	3.30
2.40	3.55	2.46	3.80	2.40	3.25	2.40	3.55
2.44	3.75	2.50	4.20	2.45	3.30	2.44	3.75
2.48	3.90	2.52	6.00	2.50	3.40	2.48	3.90
2.50	4.05	2.54	6.20	2.58	3.55	2.50	4.05
2.52	9.05	2.56	6.50	2.60	3.60	2.52	4.70
2.54	9.25	2.58	7.00	2.68	3.70	2.54	4.90
2.56	9.40	2.60	7.20	2.76	3.90	2.58	5.00
2.58	9.60	2.64	7.40	2.90	4.15	2.62	5.20
2.60	9.70	2.70	7.55	3.00	4.40	2.66	5.40
2.64	9.90	2.78	7.75	3.10	4.65	2.70	5.60
2.66	10.05	2.80	7.80	3.20	4.90	2.74	5.75
2.68	10.15	2.84	7.90	3.30	5.10	2.78	6.00
2.74	10.40	2.90	8.00	3.40	5.40	2.82	6.20
2.80	10.60	3.00	8.20	3.50	5.70	2.86	6.30

Table II 2 (contd.)

2.90	10.90	3.12	8.30	3.60	6.05	2.94	6.70
2.95	11.00	3.20	8.40	3.68	6.50	2.98	6.90
		3.28	8.50	3.72	6.70	3.00	7.00
		3.44	8.60	3.76	6.90	3.10	7.25
		3.60	8.70	3.80	7.00	3.20	7.50
		3.80	8.80	3.84	7.20	3.30	7.70
		3.90	8.90	3.88	7.30	3.40	7.85
		4.10	9.00	3.92	7.45	3.50	8.00
		4.60	9.30	4.00	7.65	3.60	8.20
		4.80	9.40	4.10	7.90	3.70	8.30
		4.90	9.50	4.20	8.10	3.80	8.50
		5.00	9.60	4.30	8.30	3.90	8.60
		5.20	9.80	4.50	8.60	4.00	8.70
		5.40	10.00	4.70	8.80	4.10	8.80
		5.60	10.15	4.80	8.90	4.20	8.90
		5.80	10.30	5.00	9.10	4.30	9.00
		6.20	10.55	5.20	9.30		(ppt.)
		6.40	10.75	5.30	9.40		
				5.50	9.60		
				5.90	10.05		
					(ppt.)		

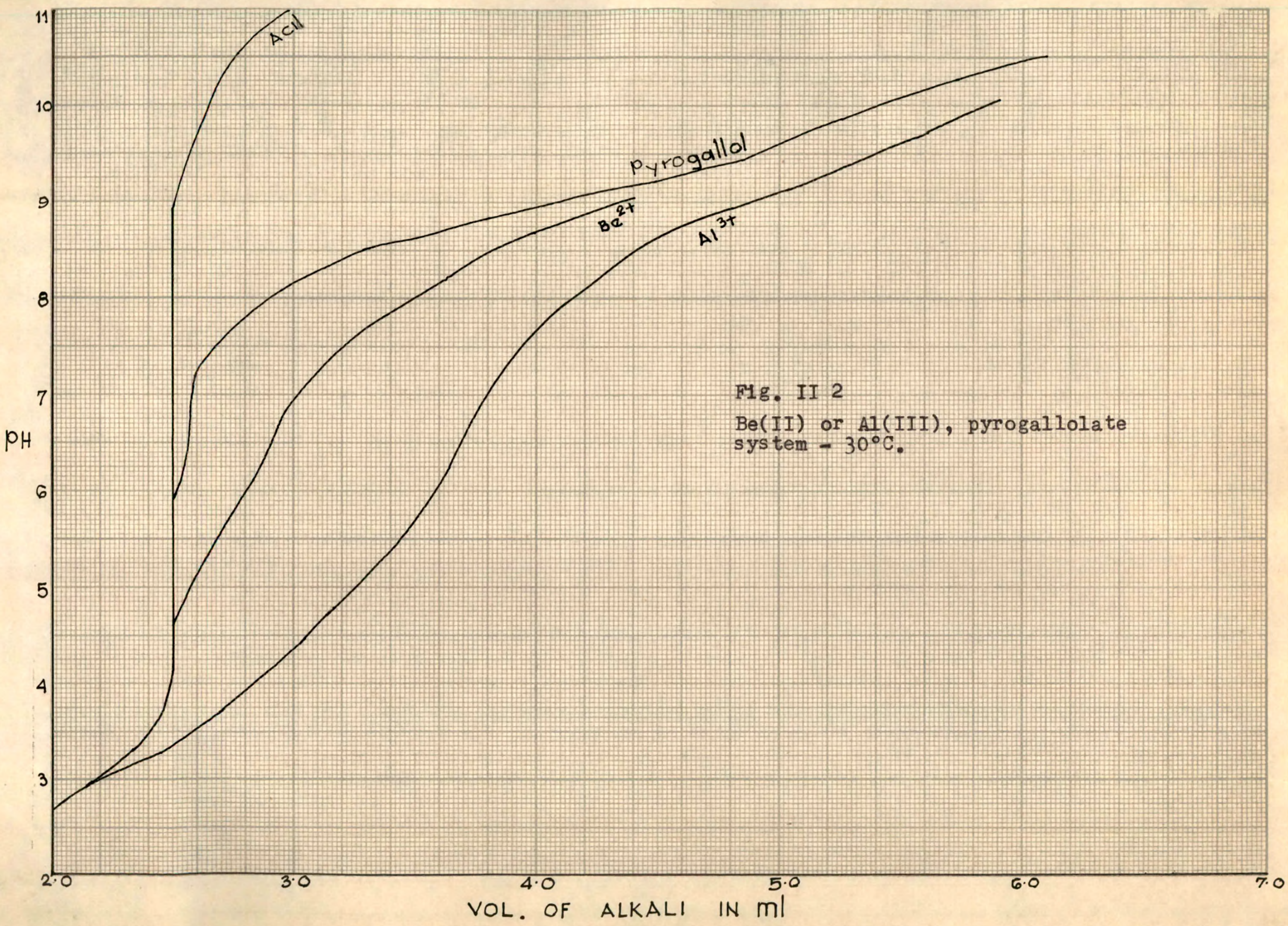


Fig. II 2

Be(II) or Al(III), pyrogallolate system - 30°C.

Table II 3

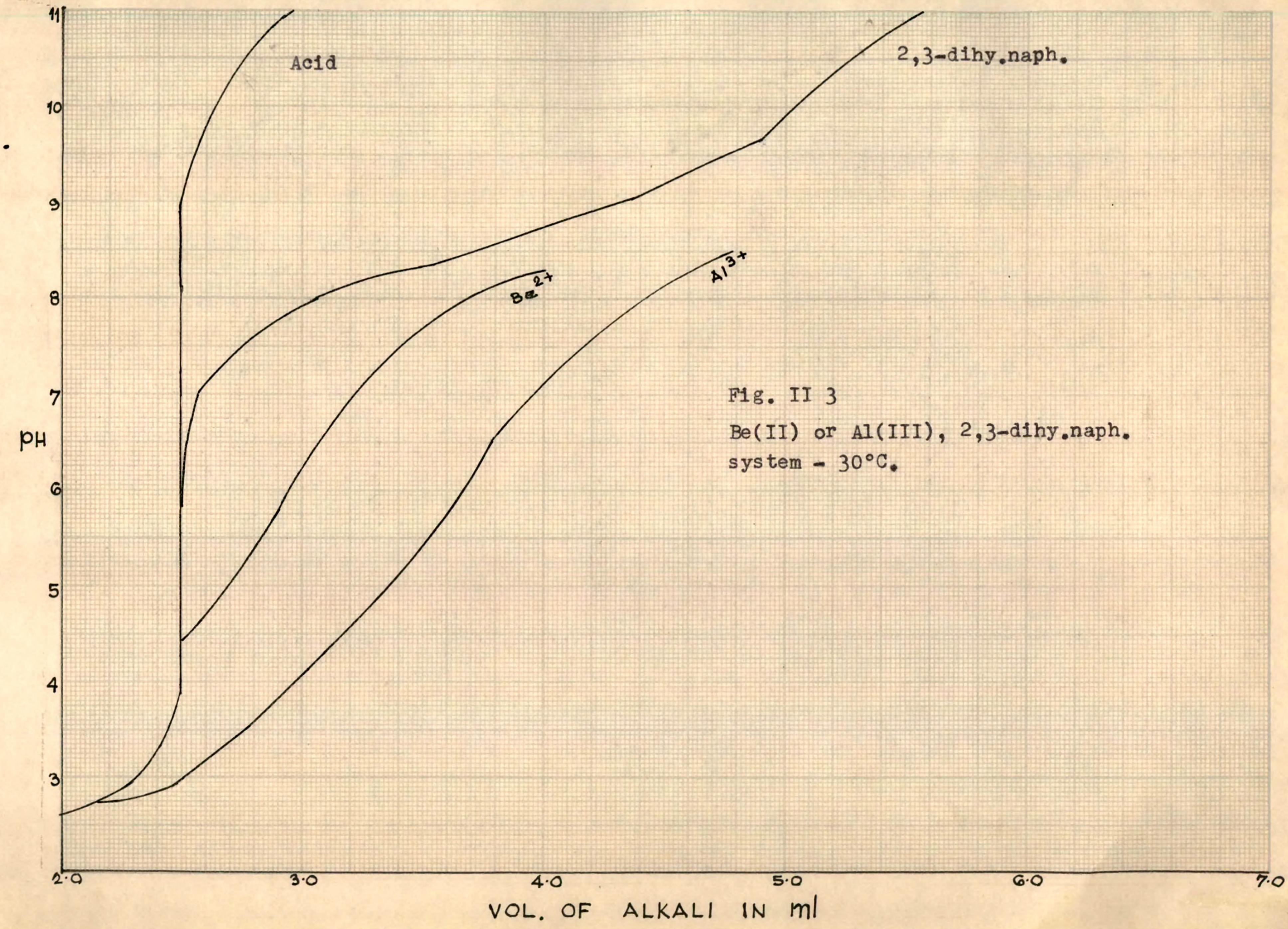
N = 0.2M V° = 50 ml. μ = 0.2M t = 30°C.

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

Perchloric acid		2,3-Dihydroxy-naphthalene		Al(III)		Be(II)		Co(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	1.70	0.00	1.70	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
2.00	2.60	2.00	2.60	2.00	2.60	2.00	2.60	2.00	2.60
2.10	2.70	2.10	2.70	2.10	2.70	2.10	2.70	2.10	2.70
2.20	2.80	2.20	2.80	2.20	2.75	2.20	2.80	2.20	2.80
2.30	2.90	2.30	2.90	2.30	2.80	2.30	2.90	2.30	2.90
2.40	3.20	2.40	3.20	2.40	2.85	2.40	3.20	2.40	3.20
2.44	3.40	2.44	3.40	2.48	2.90	2.50	3.85	2.44	3.40
2.48	3.70	2.48	3.70	2.54	3.00	2.52	4.45	2.48	3.70
2.50	3.85	2.50	3.85	2.62	3.10	2.54	4.50	2.50	3.85
2.52	9.00	2.52	6.30	2.68	3.25	2.60	4.70	2.52	6.30
2.54	9.20	2.54	6.55	2.76	3.40	2.66	4.90	2.54	6.55
2.56	9.40	2.56	6.80	2.80	3.50	2.70	5.00	2.58	6.60
2.58	9.55	2.60	7.00	2.92	3.80	2.76	5.20	2.62	6.80
2.60	9.70	2.64	7.20	3.00	3.95	2.80	5.30	2.66	6.90
2.62	9.80	2.70	7.35	3.08	4.20	2.86	5.50	2.76	7.05
2.64	9.90	2.78	7.55	3.16	4.40	2.90	5.70	2.80	7.10
2.66	10.00	2.82	7.60	3.24	4.60	2.96	6.00	2.90	7.20
2.68	10.15	2.94	7.80	3.32	4.80	3.00	6.20	3.00	7.35
2.70	10.20	2.98	7.85	3.40	5.00	3.06	6.45	3.20	7.45
2.74	10.35	3.00	7.90	3.46	5.20	3.10	6.60	3.30	7.50
2.84	10.55	3.08	8.00	3.50	5.30	3.16	6.70	3.50	7.65

Table II 3 (contd.)

2.90	10.70	3.16	8.10	3.54	5.45	3.20	6.95	3.70	7.85
2.95	10.85	3.30	8.20	3.60	5.65	3.26	7.05	3.90	8.05
3.00	11.00	3.40	8.30	3.64	5.85	3.30	7.15	4.00	8.10
		3.60	8.40	3.68	6.00	3.36	7.30	4.40	8.20
		3.90	8.60	3.72	6.20	3.40	7.45	4.60	8.30
		4.00	8.70	3.76	6.40	3.46	7.60	4.80	8.45
		4.10	8.80	3.80	6.60	3.50	7.70	5.00	8.60
		4.20	8.90	3.84	6.70	3.56	7.80	5.10	8.70
		4.50	9.20	3.88	6.80	3.66	7.90	5.20	8.80
		4.60	9.30	3.96	6.95	3.66	7.95	5.30	8.90
		4.70	9.40	4.04	7.15	3.70	8.00	5.40	9.00
		4.80	9.50	4.08	7.20	3.76	8.10	5.50	9.10
		4.90	9.60	4.12	7.30	3.80	8.15	5.60	9.30
		5.00	9.80	4.16	7.40	3.86	8.20	5.80	9.80
		5.10	10.00	4.20	7.50	3.90	8.20	5.90	10.00
		5.20	10.30	4.30	7.70	3.94	8.25	6.00	10.30
		5.30	10.50	4.40	7.90	4.00	8.30	6.10	10.50
		5.40	10.70	4.50	8.10		(ppt.)	6.20	10.70
		5.60	11.00	4.60	8.25			6.30	11.00
				4.64	8.30				
				4.72	8.40				
				4.80	8.50				
					(ppt.)				


Acid
2,3-dihy.naph.
Be2+
Al3+
Fig. II 3
Be(II) or Al(III), 2,3-dihy.naph.
system - 30°C.
pH
11
10
9
8
7
6
5
4
3
2·0
3·0
4·0
5·0
6·0
7·0
VOL. OF ALKALI IN ml

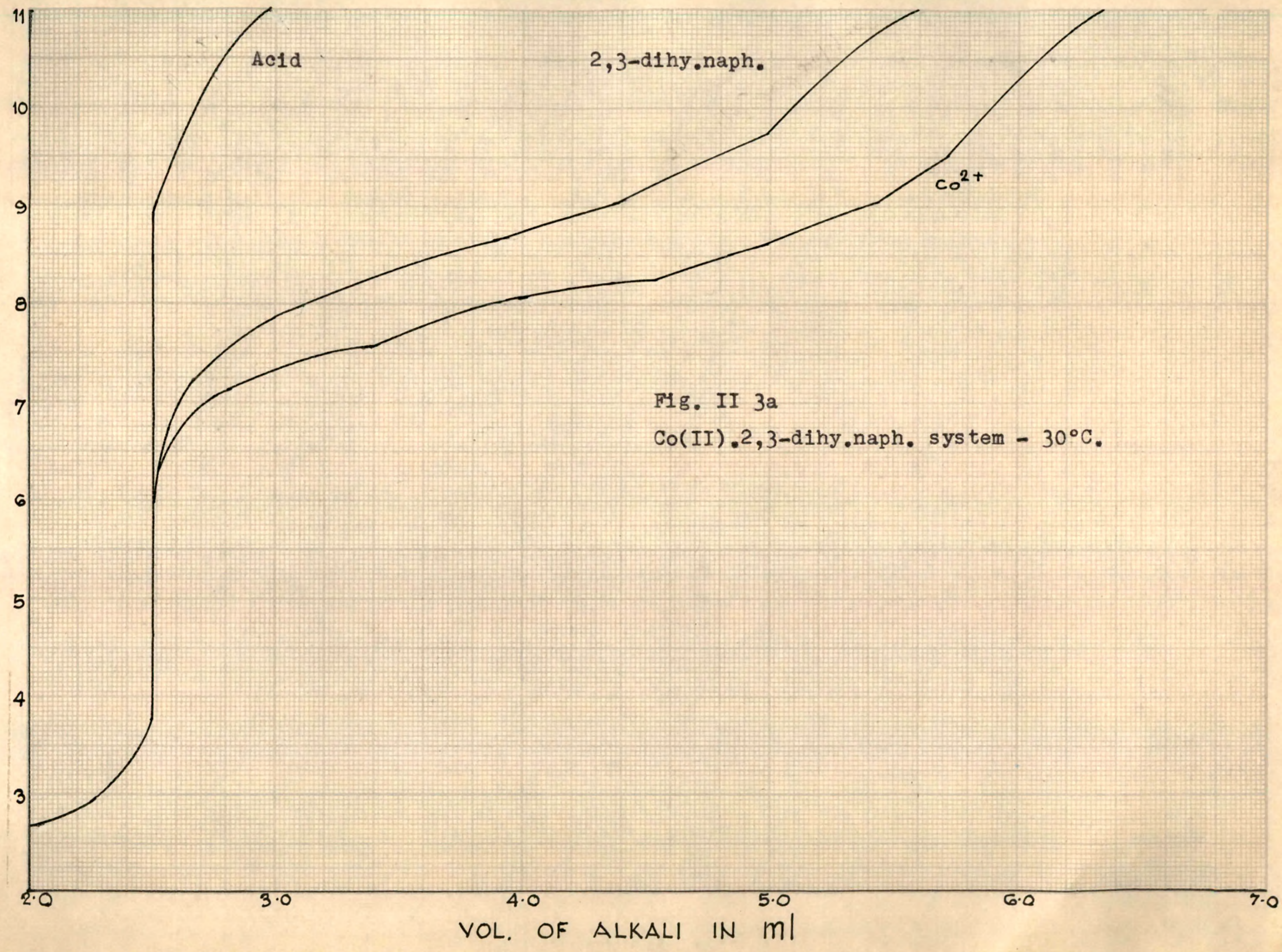


Fig. II 3a

Co(II).2,3-dihy.naph. system - 30°C.

Table II 4

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

E° = 0.01M T^{o}_{L} = 0.01M T^{o}_{M} = 0.001M

Perchloric acid		Protocatechuic acid		Al(III)		Be(II)		Co(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	1.70	0.00	1.70	0.00	1.70	0.00	1.70	0.00	1.70
1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90	1.00	1.90
1.50	2.20	1.50	2.20	1.50	2.20	1.50	2.20	1.50	2.20
2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70	2.00	2.70
2.10	2.80	2.10	2.80	2.10	2.80	2.10	2.80	2.10	2.80
2.20	2.95	2.20	2.85	2.20	2.85	2.20	2.85	2.20	2.85
2.30	3.10	2.30	2.95	2.30	2.90	2.30	2.95	2.30	2.95
2.36	3.30	2.40	3.00	2.40	2.95	2.40	3.00	2.40	3.00
2.40	3.55	2.50	3.15	2.50	3.00	2.50	3.15	2.50	3.10
2.44	3.75	2.60	3.30	2.60	3.05	2.60	3.30	2.60	3.30
2.48	3.90	2.70	3.40	2.70	3.10	2.70	3.40	2.70	3.40
2.50	4.05	2.80	3.60	2.80	3.20	2.80	3.60	2.80	3.60
2.52	9.05	2.90	3.70	3.10	3.40	2.90	3.70	2.90	3.70
2.54	9.25	3.00	3.80	3.40	3.70	3.00	3.80	3.00	3.80
2.56	9.40	3.10	3.90	3.50	3.80	3.10	3.90	3.10	3.90
2.58	9.60	3.20	4.00	3.60	3.90	3.20	4.00	3.20	4.00
2.60	9.70	3.40	4.10	3.80	4.00	3.40	4.10	3.60	4.20
2.64	9.90	3.60	4.20	3.90	4.10	3.60	4.20	4.00	4.40
2.66	10.05	3.80	4.30	4.20	4.30	3.80	4.30	4.20	4.60
2.68	10.15	4.00	4.40	4.40	4.40	4.00	4.40	4.40	4.90
2.74	10.40	4.20	4.60	4.60	4.55	4.20	4.60	4.50	5.10
2.80	10.60	4.40	4.90	4.80	4.80	4.40	4.90	4.60	5.30
2.84	10.70	4.50	5.10	5.00	5.00	4.50	5.00	4.70	5.70

Table II 4 (contd.)

2.88	10.80	4.60	5.30	5.10	5.10	4.70	5.40	4.80	6.80
2.90	10.90	4.70	5.70	5.20	5.20	4.80	5.60	4.90	7.10
2.95	11.00	4.74	6.30	5.40	5.45	4.90	5.80	5.00	7.40
		4.76	6.45	5.60	5.90	5.00	6.05	5.20	7.60
		4.80	6.80	5.70	6.20	5.10	6.20	5.30	7.70
		4.84	7.10	5.80	6.50	5.20	6.30	5.40	7.80
		4.88	7.30	5.90	6.75	5.30	6.50	5.50	7.90
		4.92	7.45	6.00	6.95	5.40	6.80	5.80	8.10
		5.00	7.60	6.10	7.20	5.50	7.05	6.20	8.40
		5.06	7.70	6.20	7.45	5.60	7.30	6.30	8.50
		5.16	7.85	6.30	7.65	5.70	7.55	6.54	8.70
		5.26	8.00	6.40	7.85	5.80	7.80	6.82	8.90
		5.30	8.00	6.50	8.05	6.00	8.15	7.16	9.10
		5.36	8.10	6.60	8.20	6.20	8.35	7.28	9.30
		5.50	8.20	6.70	8.40	6.40	8.55	7.46	9.50
		5.60	8.30	6.80	8.55	6.60	8.80	7.60	9.70
		5.70	8.40	6.90	8.70	6.70	8.90	7.74	9.90
		5.80	8.50	7.00	8.75	6.80	9.00	7.84	10.00
		5.90	8.60						
		6.10	8.70						
		6.20	8.80						
		6.30	8.90						
		6.40	9.00						
		6.60	9.10						
		6.70	9.20						
		6.80	9.40						
		6.90	9.50						
		7.00	9.60						

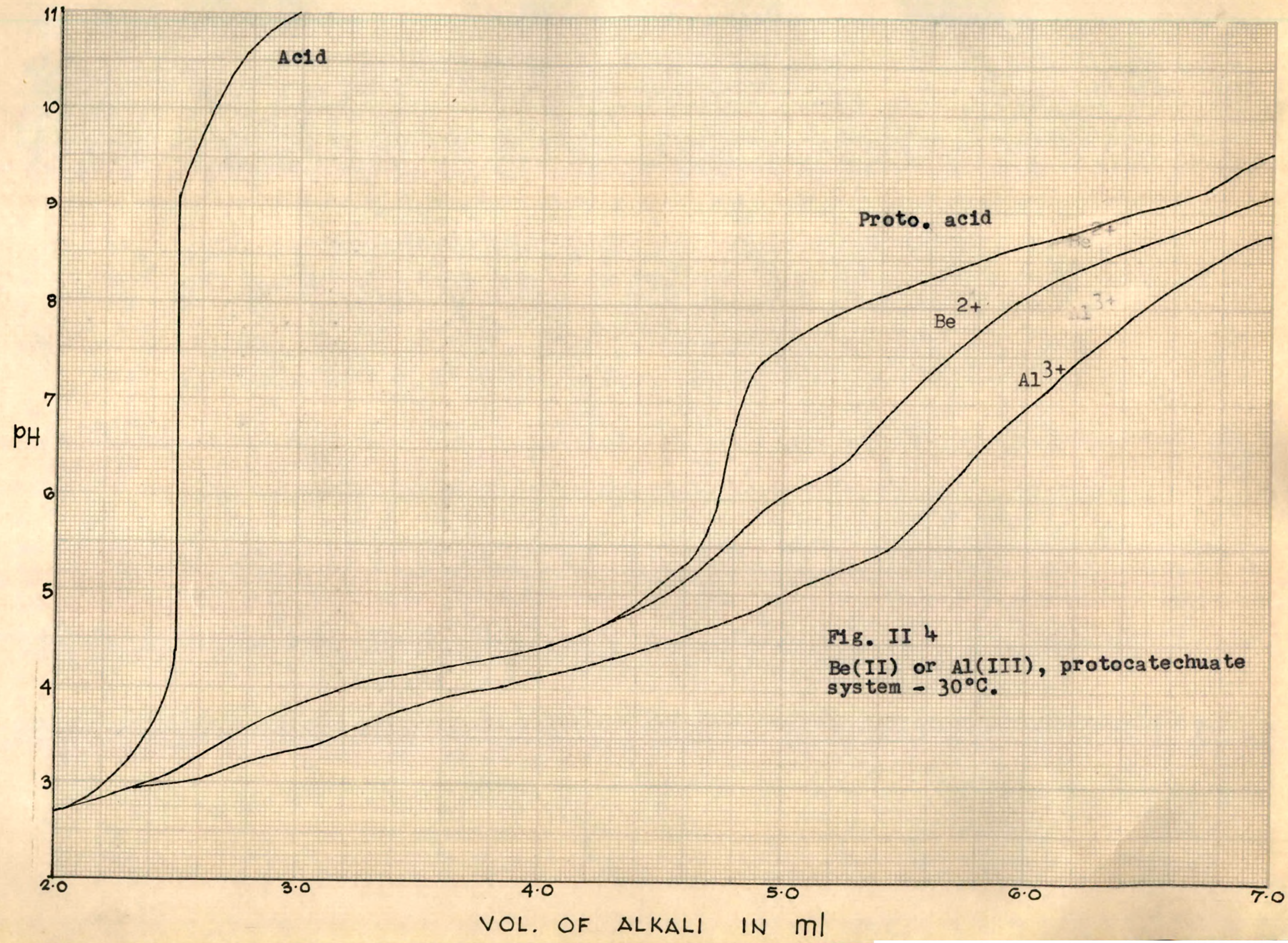


Fig. II 4

Be(II) or Al(III), protocatechuate system - 30°C.

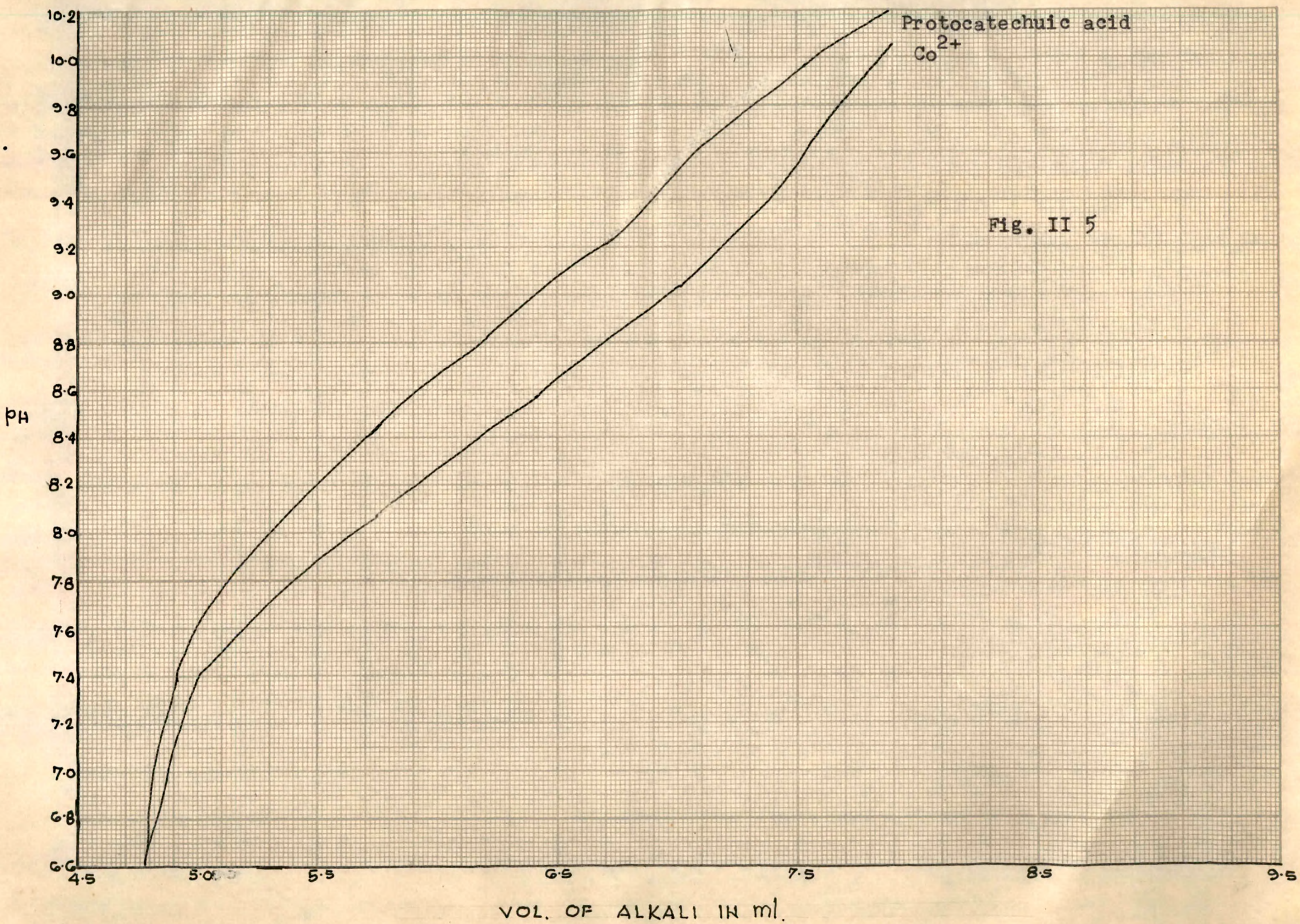

Protocatechuic acid
Co^{2+}
pH
10·2
10·0
9·8
9·6
9·4
9·2
9·0
8·8
8·6
8·4
8·2
8·0
7·8
7·6
7·4
7·2
7·0
6·8
6·6
4·5
5·0
5·5
6·5
7·5
8·5
9·5
VOL. OF ALKALI IN ml.

Fig. II 5

Table II 5

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

		Ligand (L)			
		Catechol	Pyrogallol	2,3-Dihydroxy-naphthalene	Protocatechuic acid
$\log {}^{P}K_1^H$	A	11.71	10.85	12.41	12.24
$\log {}^{P}K_1^H$	B	11.30	10.65	12.55	12.16
$\log {}^{P}K_2^H$		9.10	8.67	8.43	8.84
$\log {}^{P}K_3^H$		-	-	-	4.32

A = Values obtained using relationship $\log {}^{P}K_n^H = pH + \log \bar{n}_H/(1 - \bar{n}_H)$

B = Values obtained using relationship $\log {}^{P}K_1^H \, {}^{P}K_2^H = 2pH$ (at $\bar{n}_H = 1$).

Table II 6

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL$-\log(1-\bar{n})/\bar{n}$ data of Al-catecholate at 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	2.32	2.43	0.11	0.22_0	0.54_9	15.93_0	15.38_1
3.30	2.00_0	2.34	2.48	0.14	0.28_0	0.41_0	15.77_3	15.36_3
3.40	2.00_0	2.36	2.55	0.19	0.38_1	0.21_1	15.53_8	15.32_7
3.50	2.00_0	2.38	2.62	0.24	0.48_1	0.03_3	15.34_3	15.31_0
3.60	2.00_0	2.40	2.67	0.27	0.54_1	$\bar{1}.92_8$	15.14_6	15.21_8
3.70	2.00_0	2.44	2.74	0.30	0.60_0	$\bar{1}.82_3$	15.05_0	15.22_7
5.00	2.00_0	2.50	3.08	0.58	1.16_0	0.72_0	12.37_9	11.65_9
5.10	2.00_0	2.50	3.12	0.62	1.24_0	0.50_0	12.18_1	11.68_1
5.20	2.00_0	2.50	3.17	0.67	1.34_0	0.28_8	11.92_7	11.65_9
5.30	2.00_0	2.50	3.20	0.70	1.40_0	0.17_6	11.78_8	11.61_2
5.40	2.00_0	2.50	3.23	0.73	1.46_0	0.06_9	11.66_5	11.60_4
5.50	2.00_0	2.50	3.30	0.80	1.60_0	$\bar{1}.82_3$	11.40_3	11.58_0
5.60	2.00_0	2.50	3.34	0.84	1.68_0	$\bar{1}.67_2$	11.30_7	11.63_5

$\log K_1 = 15.30 \pm 0.08$

$\log K_2 = 11.63 \pm 0.05$

Table II 7

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL$-\log(1-\bar{n})/\bar{n}$ data of Al-pyrogallolate at 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	2.35	2.45	0.10	0.20_0	0.60_2	14.74_9	14.14_7
3.40	2.00_0	2.38	2.52	0.14	0.28_0	0.41_0	14.55_3	14.14_3
3.50	2.00_0	2.40	2.57	0.17	0.34_0	0.28_8	14.35_6	14.06_8
3.60	2.00_0	2.42	2.62	0.20	0.40_0	0.17_6	14.22_0	14.04_4
3.70	2.00_0	2.43	2.69	0.26	0.52_0	$\bar{1}.96_5$	13.96_6	14.00_1
4.60	2.00_0	2.50	3.07	0.57	1.14_0	0.78_8	12.19_6	11.40_8
4.70	2.00_0	2.50	3.10	0.60	1.20_0	0.60_2	12.02_1	11.41_9
4.80	2.00_0	2.50	3.15	0.65	1.30_0	0.36_8	11.80_7	11.43_9
4.90	2.00_0	2.50	3.20	0.70	1.40_0	0.17_6	11.60_9	11.43_3
5.00	2.00_0	2.50	3.23	0.73	1.46_0	0.09_4	11.41_4	11.32_0
5.10	2.00_0	2.50	3.29	0.79	1.58_0	$\bar{1}.85_9$	11.22_2	11.36_3

$\log K_1 = 14.07 \pm 0.07$

$\log K_2 = 11.38 \pm 0.06$

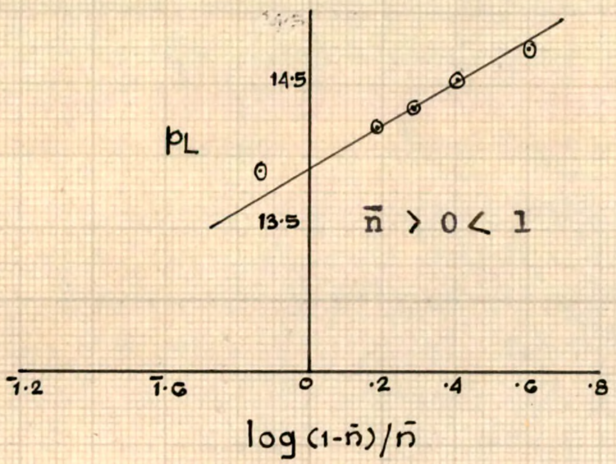


Fig. II 8

Al(III).Pyrogallolate system - 30°C.

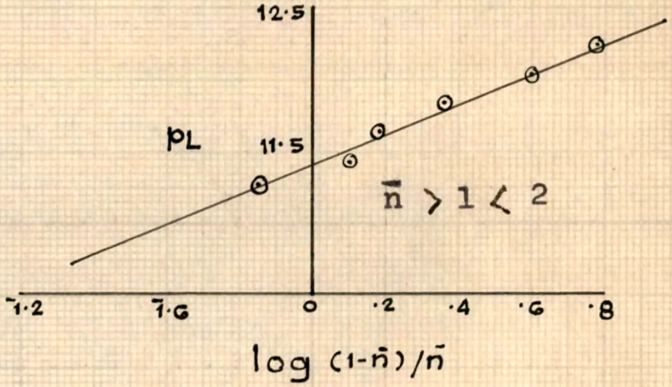


Fig. II 9

Al(III).Pyrogallolate system - 30°C.

Fig. II 6

Al(III).Catecholate system - 30°C.

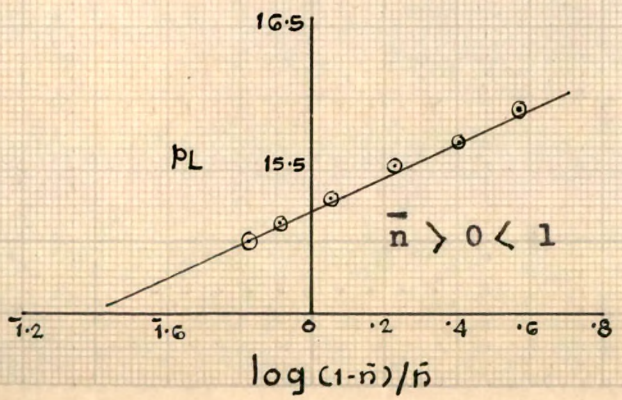


Fig. II 7

Al(III).Catecholate system - 30°C.

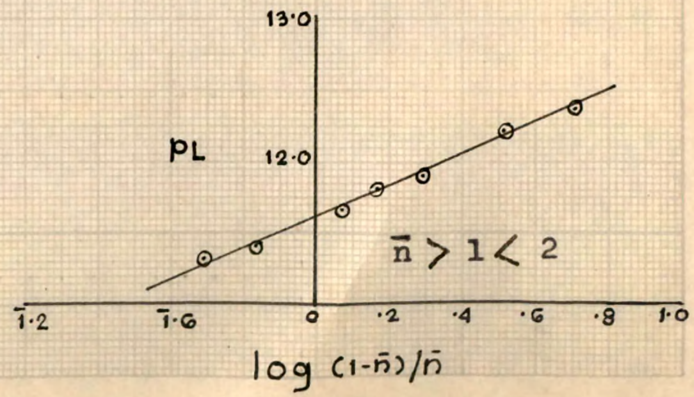


Table II 8

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Al-2,3-dihydroxy-naphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
2.80	2.00_0	2.24	2.35	0.11	0.22_1	0.54_7	17.40_9	16.86_2
2.90	2.00_0	2.30	2.45	0.15	0.29_7	0.37_4	17.21_3	16.83_9
3.00	2.00_0	2.33	2.53	0.20	0.39_3	0.18_8	17.01_8	16.83_0
3.10	2.00_0	2.35	2.60	0.25	0.49_6	0.00_6	16.82_3	16.81_7
3.20	2.00_0	2.38	2.67	0.29	0.58_1	$\bar{1}.85_8$	16.62_8	16.77_0
4.20	2.00_0	2.50	3.08	0.58	1.16_0	0.72_0	14.65_9	13.93_9
4.30	2.00_0	2.50	3.10	0.60	1.20_0	0.60_2	14.46_1	13.85_9
4.40	2.00_0	2.50	3.15	0.65	1.30_0	0.36_8	14.26_7	13.89_9
4.50	2.00_0	2.50	3.19	0.69	1.38_0	0.21_2	14.07_1	13.84_1
4.60	2.00_0	2.50	3.22	0.72	1.44_0	0.10_4	13.87_4	13.77_0
4.70	2.00_0	2.50	3.27	0.77	1.54_0	$\bar{1}.93_0$	13.68_0	13.75_0

$\log K_1 = 16.81 \pm 0.05$

$\log K_2 = 13.85 \pm 0.08$

Table II 9

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Al-protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
3.00	2.00_0	2.40	2.51	0.11	0.22_0	0.54_9	18.37_1	17.82_2
3.10	2.00_0	2.48	2.65	0.17	0.34_0	0.28_8	18.08_2	17.79_4
3.20	2.00_0	2.54	2.75	0.21	0.41_9	0.14_2	17.89_3	17.75_1
3.30	2.00_0	2.62	2.92	0.30	0.59_8	$\bar{1}.82_7$	17.61_0	17.78_3
3.40	2.00_0	2.68	3.06	0.38	0.75_7	$\bar{1}.50_6$	17.21_3	17.70_7
3.50	2.00_0	2.74	3.18	0.44	0.87_5	$\bar{1}.15_4$	16.94_6	17.79_2
5.00	2.00_0	4.44	5.00	0.56	1.08_0	1.06_0	13.17_3	12.01_3
5.10	2.00_0	4.50	5.10	0.60	1.15_5	0.73_6	12.86_2	12.12_6
5.20	2.00_0	4.56	5.21	0.65	1.25_0	0.47_7	12.75_4	12.27_7
5.30	2.00_0	4.60	5.28	0.68	1.30_7	0.35_3	12.54_7	12.19_4
5.40	2.00_0	4.64	5.36	0.72	1.38_3	0.20_7	12.34_4	12.13_7
5.50	2.00_0	4.66	5.43	0.77	1.47_9	0.03_6	12.14_1	12.10_5

$\log K_1 = 17.77 \pm 0.05$

$\log K_2 = 12.14 \pm 0.09$

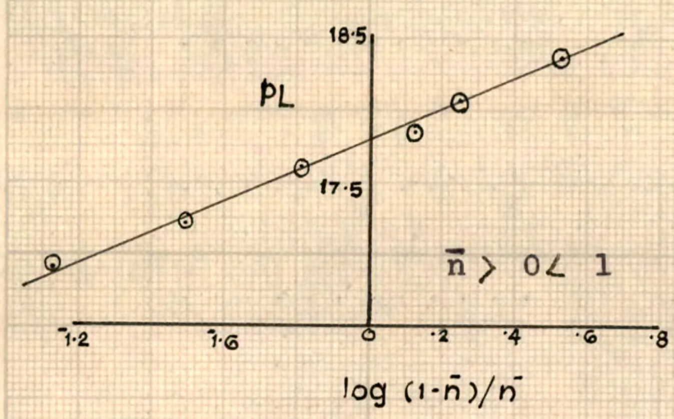
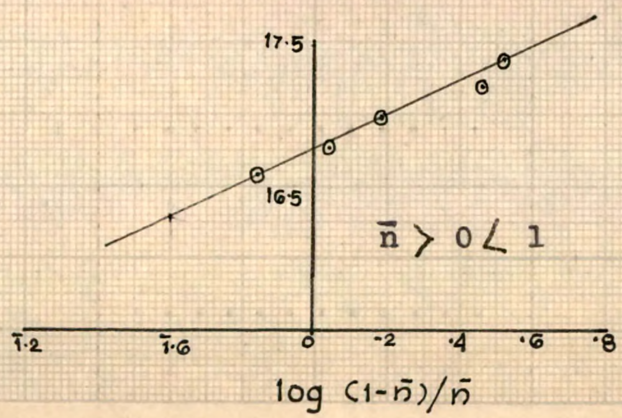


Fig. II 12

Al(III).protocatechuate system - 30°C.

Fig. II 10

Al(III).2,3-dihy.naph. system - 30°C.



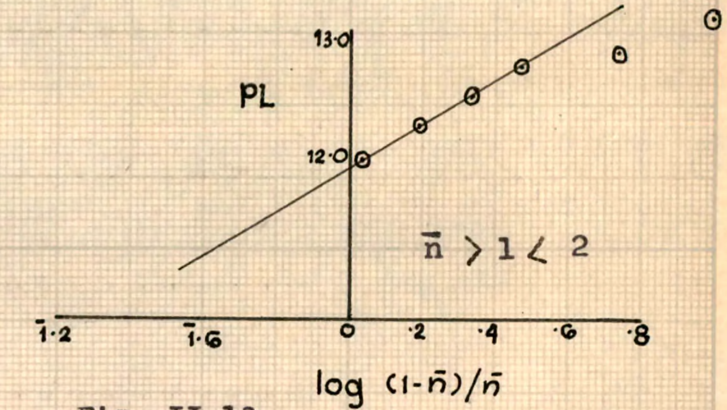


Fig. II 13

Al(III).protocatechuate system - 30°C.

Fig. II 11

Al(III).2,3-dihy.naph system - 30°C.

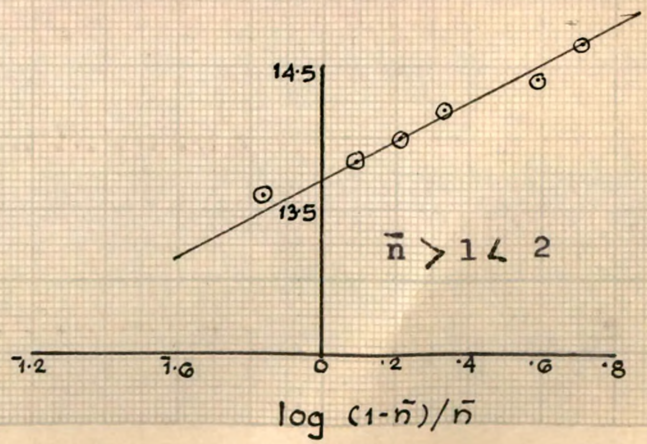


Table II 10

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Be-catecholate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.00	2.00_0	2.50	2.59	0.09	0.18_0	0.65_8	12.32_9	11.67_1
5.10	2.00_0	2.50	2.62	0.12	0.24_0	0.50_0	12.13_2	11.63_2
5.20	2.00_0	2.50	2.66	0.16	0.32_0	0.32_7	11.93_6	11.60_9
5.30	2.00_0	2.50	2.70	0.20	0.40_0	0.17_6	11.74_0	11.56_4
5.40	2.00_0	2.50	2.74	0.24	0.48_0	0.03_4	11.64_6	11.61_2
5.45	2.00_0	2.50	2.76	0.26	0.52_0	$\bar{1}.96_5$	11.54_6	11.58_1
5.50	2.00_0	2.50	2.80	3.30	0.60_0	$\bar{1}.82_3$	11.35_0	11.52_7
7.30	1.97_2	2.52	3.10	0.58	1.17_6	0.67_0	7.78_0	7.11_0
7.40	1.96_2	2.56	3.18	0.62	1.26_2	0.44_9	7.58_5	7.13_6
7.50	1.96_0	2.57	3.25	0.68	1.38_6	0.20_1	7.36_4	7.16_3
7.60	1.95_2	2.59	3.31	0.72	1.47_3	0.04_6	7.19_6	7.15_0
7.70	1.94_8	2.62	3.37	0.75	1.53_6	$\bar{1}.93_7$	7.00_0	7.06_3
7.80	1.94_4	2.64	3.44	0.80	1.64_1	$\bar{1}.74_8$	6.92_7	7.17_9
7.90	1.93_6	2.66	3.50	0.84	1.73_0	$\bar{1}.56_8$	6.73_8	7.17_0

$\log K_1$ = 11.61 ± 0.06
$\log K_2$ = 7.12 ± 0.05

Table II 11

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Be-pyrogallolate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
5.40	2.00_0	2.50	2.65	0.15	0.30_0	0.36_8	10.55_3	10.18_5
5.50	2.00_0	2.50	2.67	0.17	0.34_0	0.28_8	10.35_8	10.07_0
5.60	2.00_0	2.50	2.69	0.19	0.38_0	0.21_2	10.16_1	9.94_9
5.70	2.00_0	2.50	2.72	0.22	0.44_0	0.10_4	9.96_4	9.85_0
5.80	2.00_0	2.50	2.79	0.29	0.58_0	$\bar{1}.85_9$	9.77_0	9.91_1
6.00	2.00_0	2.50	2.80	0.30	0.60_0	$\bar{1}.82_3$	-	-

$\log K_1$ = 9.99 ± 0.09

Table II 12

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data of Be-2,3-dihydroxynaphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
4.80	2.00_0	2.50	2.62	0.12	0.24_0	0.50_0	13.41_2	12.91_2
4.90	2.00_0	2.50	2.66	0.16	0.32_0	0.32_7	13.21_6	12.88_9
5.00	2.00_0	2.50	2.69	0.19	0.38_0	0.21_2	13.01_9	12.80_7
5.10	2.00_0	2.50	2.71	0.21	0.42_0	0.14_0	12.82_1	12.68_1
5.20	2.00_0	2.50	2.75	0.25	0.50_0	0.00_0	12.62_5	12.62_5
5.30	2.00_0	2.50	2.80	0.30	0.60_0	$\bar{1}.82_3$	12.43_0	12.60_7
5.40	2.00_0	2.50	2.82	0.32	0.64_0	$\bar{1}.75_0$	-	-

$\log K_1 = 12.77 \pm 0.09$

Table II 13

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data of Be-protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
5.60	2.00_0	4.68	4.78	0.10	0.19_2	0.62_4	11.73_0	11.10_6
5.70	2.00_0	4.70	4.82	0.12	0.23_0	0.52_4	11.66_8	11.14_4
5.80	2.00_0	4.71	4.88	0.17	0.32_6	0.31_5	11.46_7	11.15_2
5.90	2.00_0	4.72	4.92	0.20	0.38_3	0.20_7	11.36_9	11.16_2
6.00	2.00_0	4.72	4.96	0.24	0.46_0	0.06_9	11.17_1	11.10_2
6.10	2.00_0	4.74	5.05	0.31	0.59_4	$\bar{1}.83_4$	10.97_5	11.14_1
6.20	2.00_0	4.75	5.13	0.38	0.72_8	$\bar{1}.57_2$	10.68_0	11.10_8

$\log K_1 = 11.13 \pm 0.03$

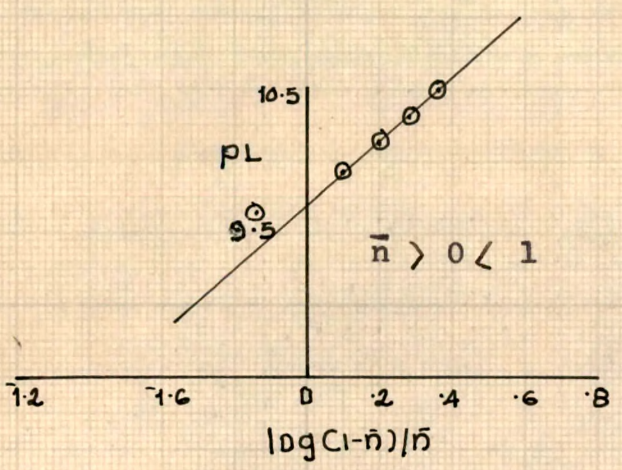


Fig. II 16

Be(II).pyrogallolate system - 30°C.

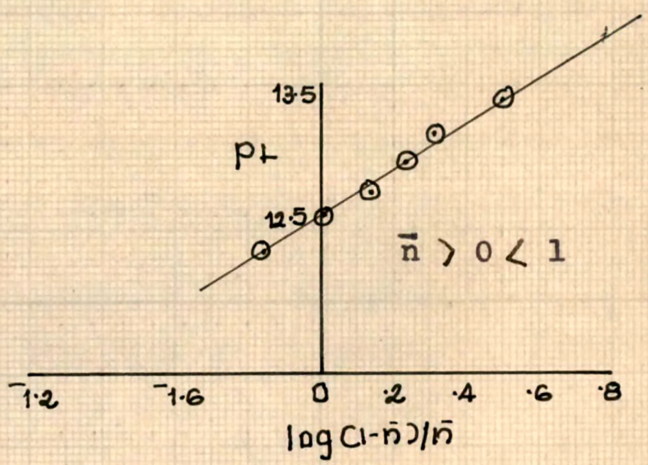


Fig. II 17

Be(II).2,3-dihy.naph. system - 30°C.

Fig. II 14

Be(II).Catecholate system - 30°C.

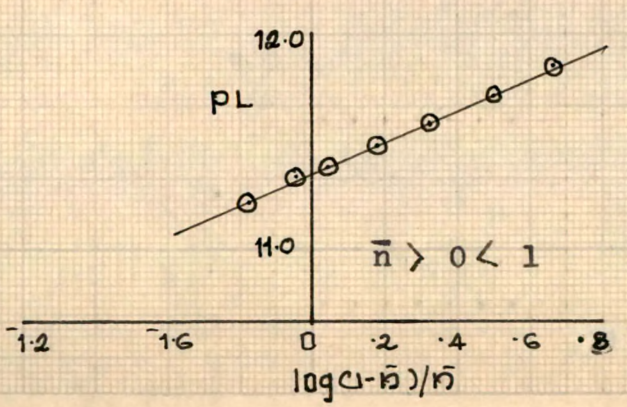


Fig. II 15

Be(II).catecholate system - 30°C.

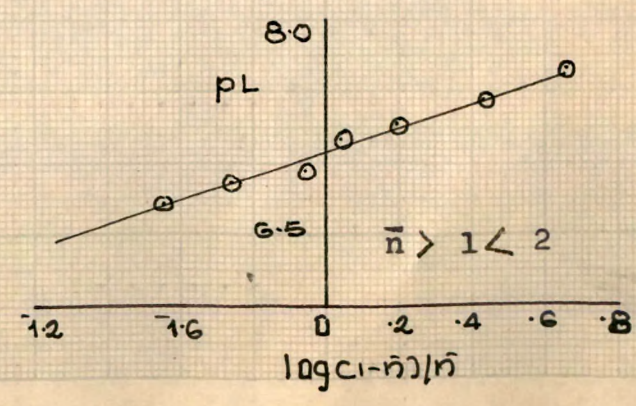


Table II 14

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Co-catecholate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
7.00	1.98_2	2.56	2.58	0.02	0.04_0	1.38_0	8.42_3	7.04_3
7.10	1.98_0	2.56	2.60	0.04	0.08_0	1.06_0	8.12_5	7.06_5
7.20	1.97_6	2.56	2.63	0.07	0.14_1	0.78_4	7.92_6	7.14_2
7.30	1.97_2	2.56	2.65	0.09	0.18_2	0.65_2	7.72_0	7.06_8
7.40	1.96_2	2.58	2.70	0.12	0.24_4	0.49_1	7.53_1	7.04_0
7.50	1.96_0	2.58	2.74	0.16	0.32_6	0.31_5	7.33_6	7.02_1
7.60	1.95_2	2.60	2.78	0.18	0.36_8	0.23_4	7.13_6	6.90_2
7.70	1.94_8	2.62	2.90	0.28	0.57_3	$\bar{1}.87_2$	6.94_6	7.07_4

$\log K_1 = 7.04 \pm 0.09$

Table II 15

B, $\bar{n}_H$, $\bar{n}$, $\log(1-\bar{n})/\bar{n}$, pL and pL-$\log(1-\bar{n})/\bar{n}$ data of Co-2,3-dihydroxy-naphthalene at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	$\log(1-\bar{n})/\bar{n}$	pL	pL-$\log(1-\bar{n})/\bar{n}$
6.90	1.96_8	2.58	2.66	0.08	0.16_2	0.71_3	9.29_0	8.57_7
7.00	1.96_4	2.59	2.72	0.13	0.26_4	0.44_5	9.04_9	8.60_4
7.10	1.94_8	2.63	2.79	0.16	0.32_7	0.31_3	8.89_0	8.57_7
7.20	1.93_6	2.66	2.89	0.23	0.47_3	0.04_6	8.65_0	8.60_4
7.30	1.93_2	2.67	2.93	0.26	0.53_6	$\bar{1}.93_7$	8.45_9	8.52_2
7.40	1.91_2	2.72	3.06	0.34	0.70_8	$\bar{1}.61_5$	8.17_6	8.56_1
7.60	1.87_2	2.82	3.42	0.60	1.27_3	0.42_5	7.88_0	7.45_5
7.70	1.85_2	2.87	3.52	0.65	1.39_3	0.18_8	7.60_1	7.41_3
7.80	1.82_4	2.94	3.64	0.70	1.52_1	$\bar{1}.96_3$	7.32_7	7.36_4
7.90	1.79_2	3.02	3.74	0.72	1.59_1	$\bar{1}.84_0$	7.25_0	7.41_0
8.00	1.77_3	3.07	3.83	0.76	1.69_6	$\bar{1}.64_0$	7.08_1	7.44_1

$\log K_1 = 8.57 \pm 0.03$

$\log K_2 = 7.43 \pm 0.07$

Fig. II 20

Co(II). 2,3-dihy.naph. system - 30°C.

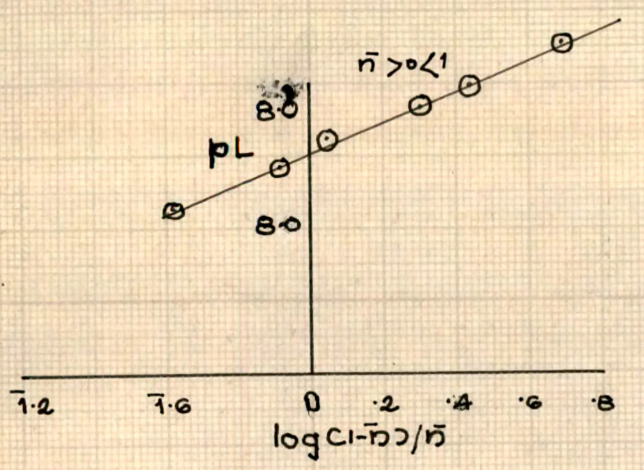


Fig. II 21

Co(II). 2,3-dihy.naph. system - 30°C.

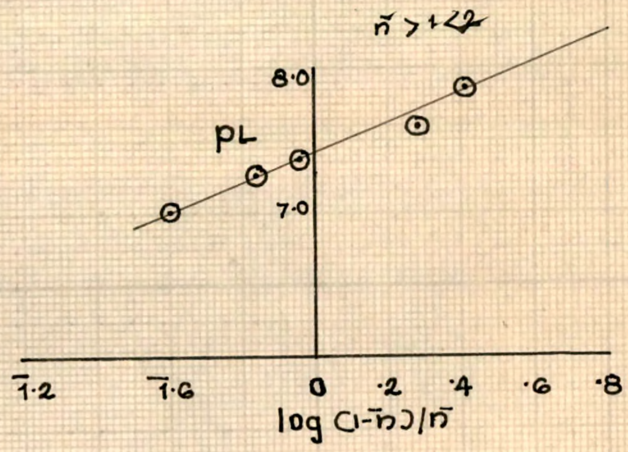


Fig. II 18

Be(II). protocatechuate system - 30°C.

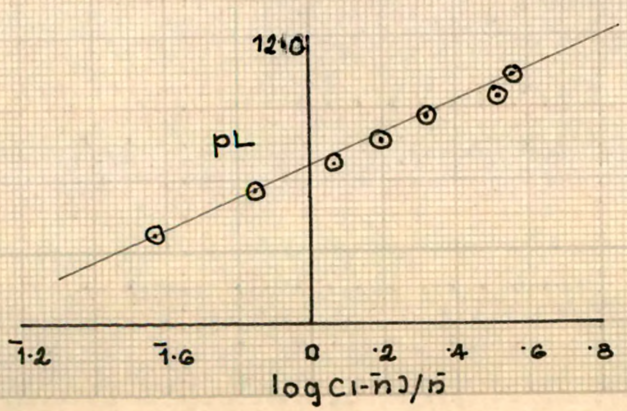


Fig. II 19

Co(II). catecholate system - 30°C.

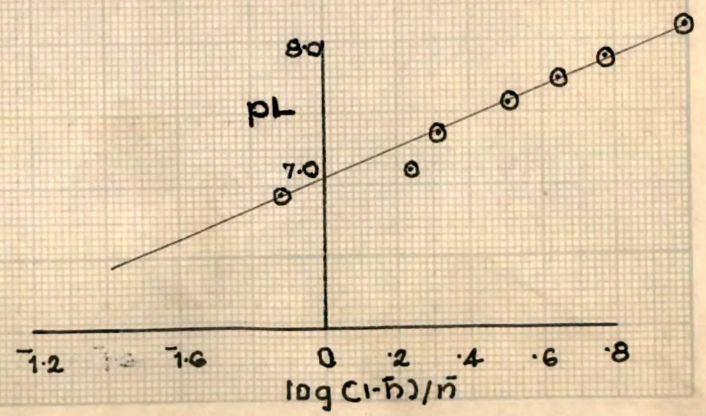


Table II 16

B, $\bar{n}_H$, $\bar{n}$, log(1-$\bar{n}$)/$\bar{n}$, pL and pL-log(1-$\bar{n}$)/$\bar{n}$ data of Co-protocatechuate at 30°C.

B	$\bar{n}_H$	V"	V"'	V"'-V"	$\bar{n}$	log(1-$\bar{n}$)/$\bar{n}$	pL	pL-log(1-$\bar{n}$)/$\bar{n}$
7.40	2.00_0	4.90	5.00	0.10	0.19_1	0.62_6	8.26_1	7.63_5
7.50	2.00_0	4.94	5.06	0.12	0.22_9	0.52_7	8.11_0	7.57_3
7.60	1.94_9	5.00	5.19	0.19	0.37_2	0.22_7	7.90_8	7.68_1
7.70	1.93_5	5.06	5.29	0.23	0.45_3	0.08_1	7.69_4	7.61_3
7.80	1.93_5	5.12	5.39	0.27	0.53_1	$\bar{1}.94_6$	7.60_6	7.66_0
8.50	1.68_0	5.80	6.30	0.50	1.12_0	0.87_5	6.26_6	5.39_1
8.60	1.60_0	5.90	6.41	0.51	1.19_7	0.61_0	6.05_9	5.44_9
8.70	1.56_0	6.02	6.54	0.52	1.24_9	0.47_9	5.94_7	5.46_8
8.80	1.52_0	6.18	6.70	0.52	1.27_8	0.41_4	5.79_5	5.38_1
8.90	1.48_0	6.30	6.82	0.52	1.31_0	0.34_7	5.63_3	5.28_6

$\log K_1 = 7.63 \pm 0.06$

$\log K_2 = 5.41 \pm 0.09$

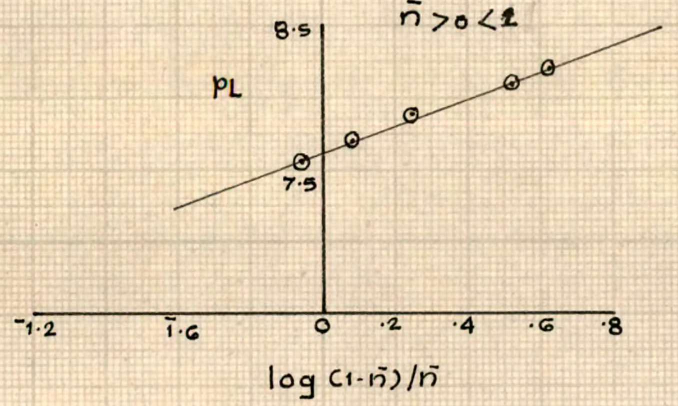


Fig. II 22

Co(II).protocatechuate system - 30°C.

Fig. II 23

Co(II).protocatechuate system - 30°C.

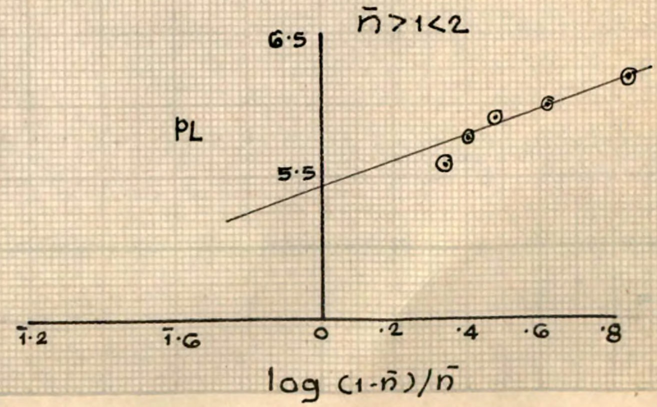


Table II 17

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

Ligand (L)		Metal ions				
		Aluminium(III)	*Copper(II)	Beryllium(II)	*Nickel(II)	Cobalt(II)
Catechol	$\log K_1$	15.30 ± 0.08	12.97 ± 0.06	11.61 ± 0.06	7.80 ± 0.03	7.04 ± 0.09
	$\log K_2$	11.63 ± 0.05	-	7.12 ± 0.05	-	-
Pyrogallol	$\log K_1$	14.07 ± 0.07	12.88 ± 0.04	9.99 ± 0.09	7.07 ± 0.06	-
	$\log K_2$	11.38 ± 0.06	-	-	-	-
2,3-Dihydroxy-naphthalene	$\log K_1$	16.81 ± 0.05	14.42 ± 0.03	12.77 ± 0.09	9.72 ± 0.07	8.57 ± 0.03
	$\log K_2$	13.85 ± 0.08	-	-	-	7.43 ± 0.07
Protocatechuic acid	$\log K_1$	17.77 ± 0.05	14.17 ± 0.08	11.13 ± 0.03	8.77 ± 0.05	7.63 ± 0.06
	$\log K_2$	12.14 ± 0.09	-	-	-	5.41 ± 0.09

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

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