CHAPTER 2

Formation constants of some ternary complexes involving tertiary diimines and O^- - O coordinating ligands.

page

2.1 Introduction of the study of the stability of ternary complexes.

It is evident from the discussion in earlier chapter that the electronic characterstics of the ligands decide the nature of M-L interaction and hence play a major role in stabilizing the ternary complexes.

It had been recognized several years ago that the presence of an aromatic amine is crucial for high stability of a ternary complex[1]. This has been repeatedly confirmed[2-9] and was attributed to π back bonding from the metal ion to the aromatic amine[1, 5, 9.]. If a complex MA is considered, where A is a tertiary diimine like 2,2' - bipyridine, N→M σ bond formation results in the shift of electron density from ligand to metal. Because of the increase in electron density over the metal ion, it behaves as a better π electron donor. The tertiary diimine having vacant π antibonding orbitals can behave as a better π acceptor on donation of N electron pair to the metal ion. This facilitates π bond formation between the filled $d\pi$ orbitals of the metal and vacant π antibonding orbitals over the diimine ligand. Thus, there is synergic stabilization of N → M σ bond and M → A π bond. The d_π - p_π interaction does not allow the electron density over the metal ion to increase significantly. In other words the electronegativity of $[MA]^{2+}$ is almost same as $[M(H_2O)_n]^{2+}$ and hence $K^{MA}_{MAL} \approx K^{M}_{ML}$. In case of [M bipy L] type of complexes where L = anion, the effect of π bonding, less electrostatic repulsion and charge neutralization favours the formation of [M bipy L] than $[ML_2]$.

The M → A π interaction results in the shift of π electron density from metal to ligand. This results in an increase in class A character of a transition metal ion on coordination with a tertiary diimine. This brings in discriminating

behaviour [5, 10-12] in MA towards the secondary ligand L coordinating through N-N, N-Ō or Ō-Ō, as observed by Sigel and coworkers [5,10] and Bhattacharya and coworkers [11,12]. The effect is more significant in the complexes of copper (II) and the value of Δ log K in [Cu A Ō-Ō] complex is positive [10,11] (Table 1.2).

According to Sigel the higher stabilization in [Cu A Ō-Ō] can be attributed to two reasons, (1) The distorted octahedral structure of [Cu $(H_2O)_6$]$^{2+}$, due to Jahn-Teller effect [5], gets some what more distorted towards a square planar structure on coordination with a strongly coordinating bipyridyl ligand, and creates the right geometry for the coordination of a second ligand in the square plane. Another explanation is in terms of the "cooperative effects" [5, 8, 13] between the π orbitals of the two ligands [14] mediated through the metal $d\pi$ electrons. The overall delocalization is supposed to stabilize the ternary complex to a greater extent.

Positive value of Δ log K in [Cu (bipy) (malonate)] [5, 12, 15] and less negative values of Δ log K in Cu (bipy) L with L = N-Ō ligand like glycine [12], does not support the "cooperative π interaction" because malonate or glycinate are only σ bonding ligands. Bhatthacharya and coworkers have shown that the interligand π interaction mediated through metal ion, is not so significant and have extended an alternate explanation in terms of electron repulsion [12, 16, 17.] In the formation of binary complexes, there is repulsion between the metal $d\pi$ electrons and the additional lone pairs of electrons present over the Ō-Ō coordinating ligand. In the ternary complex, M → A π bonding reduces the electron density over the metal ion and hence the lone pair of electrons over L has to face less repulsion while combining with MA^{2+} than with the free metal ion. The effect is maximum in case of Ō-Ō coordinating ligands like pyrocatecholate ion with lone pair of electrons over both Ō. This results in $K^{\text{Cu bipy}}_{\text{Cu bipy cat}} >$

$K^{Cu}_{Cu\ cat}$ or the positive value of $\Delta \log K$ [10, 11].

Basic understanding of the above observation has pointed out that (1) the π acidity of a tertiary diimine ligand has utmost importance in deciding the preference of the metal for a second ligand with specific characteristics. Hence, the substituents over A which are not involved in coordination but which affect the π acidity of the ligand should be expected to have effect on the stability of the ternary complex. (2) The substituents on the secondary ligands which alter the basicity or electron density over the coordinating site should also have influence on the stability of the complex.

It was concluded on the basis of the observation made by various groups of workers that the stability of the ternary complex depends crucially on the π - accepting qualities of the hetero aromatic N base [8, 17, 18]. The influence of the π acceptor capability of the amine can be seen in Table[2.1.1]. Electronic spectra, ESR parameters [13] and CD studies [19] have provided further evidence for π back bonding and the transmission of electronic effects through bonding orbitals in mixed ligand complexes[20, 21].

Study of M (dpx) (pyrocatecholate) complexes[22] of the later members of the first transition series where dpx = bis (2-pyridyl) amine (dpa), bis (2-pyridyl) ketone (dpk) or bis (2-pyridyl) methane (dpm) has shown that the tendency for the formation of ternary complexes decreases within the series dpk > dpm > dpa. This is because dpk with $>C = O$ having sp^2 hybridized carbon and electron withdrawing mesomeric effect can act as the best π accepting ligand among the three, whereas dpa with electron releasing > NH group has least π accepting tendency and hence it forms least stable complexes.

Table 2.1.1

Influence of the π acceptor capability of the amine in (amine) Cu (pyrocatecholate) complexes [Ref.8] ; I=0.1, $NaClO_4$; 25°C.

Amine Ligand	Δ log K	log x	$pK^{H}_{H_2A.}$	$pK^{H}_{HA.}$
2,2' - Bipyridyl	+ 0.43	6.15	- 0.2	4.49
4 - (2'-pyridyl) imidazole	+ 0.11	5.47	1.33	5.49
2 - Picolyl amine	- 0.11	4.64	2.05	8.70
4 - Aminomethylimidazole	- 0.35	3.46	4.73	9.35
Ethylenediamine	- 0.76	2.65	7.10	9.89

In another series of tertiary diimines, Bhattacharya and coworkers [11, 12] [17, 23] have observed that the tendency of mixed ligand formation follows the order 2(2'-pyridyl) benzimidazole $>$ 2,2'-bipyridyl $\approx$ 1,10-phenanthroline $>$ 2(2'-pyridyl) imadazoline. Because of the benzimidazole part which is a better π acceptor than pyridine Cu $\rightarrow$ A π intraction is greater in the complexes containing 2(2'-pyridyl) benzimidazole. This results in greater stabilization of the ternary complex. The saturated imidazoline ring in 2(2'-pyridyl) imidazoline can not have π interaction with the metal ion and hence results in less stable ternary complex. Similar observations have been made in the series of complexes consisting of 2,2'-bipyridyl, 1,10-phenanthroline and 5-nitro-1,10-phenanthroline as primary ligands [24]. (Table 2.1.2).

The substituents over the secondary ligands, though not coordinated with the metal ion, also influence the stability of the ternary complex. The complexes containing aromatic amines and pyrocatechol derivatives have been studied by Bhattacharya and coworkers [23,24] and also by Sigel and coworkers [25]. Some, typical results are summarised in Table [2.1.3.]. The effect of bipyridyl analogues has also been studied on the stability of ternary complexes involving copper (II) and substituted o-hydroxy aldehydes. Both groups conclude that the electron density over the ligand (L) with $\bar{O}$-$\bar{O}$ as donor site has significant influence on the stability of the ternary [Cu A L] complexes. Electron withdrawing substituents on L lower the stability of the complex and electron donating substituents increase it.

For further investigation of the effect of substituents and nature of both the primary and the secondary ligands on the stability of ternary complexes, three series of complexes have been considered in the present work. One series

Table 2.1.2

Stability contants of ternary complexes.

(tertiary diimine) Cu (pyrocatecholate) [Ref. 23, 24], 50% aq. dioxane ; I = 0.2, $NaClO_4$; $30^{o}C$.

Tertiary diimine Ligand	Log K	Δ Log K
2,2' - Bipyridyl	13.60	+ 0.80
1,10 - Phenanthroline	13.48	+ 0.68
5 - Nitro - 1, 10 - Phenanthroline	13.76	+ 0.96
Bis (2 - pyridy) amine	13.58	+ 0.78
Di - (2 - pyridy) ketone	14.65	+ 1.85
2, (2' - pyridyl) benzimidazole	14.12	+ 1.32
2, (2' - pyridyl) imidazoline	12.33	- 0.47

Table 2.1.3

Stability constants of ternary complexes Cu (2,2' - bipyridyl) L [Ref. 23,24] ; 50% aq. dioxane , I = 0.2, $NaClO_4$; 30°C.

Ligand L	Log K	Δ Log K
Pyrocatechol	13.6	+ 0.80
Tiron	14.39	- 0.02
Protocatechuic acid	15.04	- 0.37
Pyrogallol	15.04	- 0.52
1,8 - Dihydroxynaphthalene	9.05	- 1.52
2,3 - Dihydroxynaphthalene	14.92	+ 0.37
Catecholaldehyde	14.13	+ 0.28
Dopamine	13.94	- 0.06
Adrenaline	15.27	+ 0.61

consists of substituted o-hydroxy aromatic aldehydes (L^1-L^5) as secondary ligands, second series involves derivatives of bidentate β-ketoanilides (L^6-L^9) and the third consists of the amides derived from salicylic acid (L^{10}-L^{12}). The primary ligands used are bis (2-pyridyl) amine (A^1) and 5-nitro-1,10-phenanthroline (A^2). The results have been compared with the earlier reports with corresponding 2,2'-bipyridyl and 1,10-phenanthroline systems. The solution stabilities have also been correlated with the electronic spectra of the complexes.

2.2 Experimental.

Chemicals · The ligands bis (2-pyridyl) amine (Fluka AG), 5-nitro-1,10-phenanthroline (Sigma), acetoacetanilide, acetoacet-o- toluedide, acetoacet-o-anisidide (C and C chemicals division, New York). Salicylamide (Riedel) and salicylanilide (BDH) were of A.R. grade. All these reagents were used as received. Salicylaldehyde which was reagent grade, was purified by distillation. 1,4 - Dioxane * was purified according to the literature method [26] prior to use as a solvent in potentiometric titrations.

Synthesis of ligands ·

5-Nitro Salicylaldehyde was prepared by the method of Dandegaonkar and shet 27, m.p. 127°C (Reported 126-127°C).

5-Bromosalicylaldehyde was prepared by low temparature (< 5° C) bromination of salicylaldehyde by liquid bromine in acetic acid. The product was separated after addition of the reaction mixture to cold water and recrystallised twice from ethanol ; m.p. 107°C (Reported [28] 105-107°C).

5-Bromosalicylamide was prepared by the bromination of salicylamide with N-bromosuccinimide in DMF, susequent treatment with water to remove succinic acid and recrystallization from petroleum ether (40-60°). m.p. 232°C (Reported [29] 232°C). Benzoyl acetanilide was prepared according to the literature method [30]. m.p. 106° (Reported 106-106.5°C).

* Here onwards through out the text, the term dioxane refers to 1, 4-dioxane.

Copper perchlorate was prepared from analytically pure copper carbonate by treatment with 70% perchloric acid (A.R.). The resulting soild was vacuum filtered, washed with ethanol till it was free from excess acid and recrystallized several times from ethanol. (Copper perchlorate is partially soluble in alcohol).

Stock solution of copper perchlorate, perchloric acid, sodium hydroxide and sodium perchlorate were all prepared in (carbonate free double distilled) deionized water. Copper perchlorate solution was standardized by complexometric titration with standard EDTA solution using pyrocatechol violet as indicator [31]. Sodium perchlorate solution was prepared from analytically pure monohydrate. Carbonate free sodium hydroxide solution was prepared according to the literature method [32] and standardized by potentiometric titration with standard oxalic acid solution. Standard perchloric acid solution was prepared from A.R. 70% acid by proper dilution and titration with standard alkali.

Fresh solution of ligands having appropriate concentrations were prepared every time from the pure compounds in purified dioxane.

Potentiometric determination of the stability constants

Irving-Rossotti titration technique [33] and its extension [9] in the cases of ternary complexes has been used to determine the preliminary values of the protonation constants of the ligands, formation constants of binary complexes and the formation constants of the ternary complexes.

The solutions containing appropriate amounts of standard perchloric acid, sodium perchlorate and ligand and metal solutions were titrated, potentiometrically, against standard (0.20 M) sodium hydroxide solution. In all the cases acid concentration was kept 2.0×10^{-2} M and the total ionic strength (I) of the

solutions was maintained at 0.2 M with the help of standard sodium perchlorate solution. For the determination of protonation constants of the ligands, ligand soultions of 2.0×10^{-3} or 5.0×10^{-3} M concentrations were used, where as for the determination of the formation constants of the binary complexes the solutions having $[M^{2+}] = 1.0 \times 10^{-3}$ M and $[LH] = 5.0 \times 10^{-3}$ M were used. Solutions containing M^{2+} and primary and secondary ligands in 1:1:1 ratio, concentration of each being 1.0×10^{-3} M, were titrated for derterminıng the formation constants of the ternary complexes. Medium for all the titrants was 50% (v/v) aqueous dioxane and the temparature was maintained at $30 \pm 1^{o}C$ during the progress of the titrations.

The titrations were carried out using a digital pH meter (DIGICHEM -8201) having on accuracy of $\pm$ 0.01 and a Toshniwal combination glass electrode.

Observed values of the pH were corrected to get the concentration of hydrogen ion in the solution. For this pH values of standard perchloric acid solutions have been determined under the experimental conditions and compared with theoretical values. This difference takes into account liquid junction potential across the membrane and effect of the ionic strength of the medium [34]. The constant difference has been considered as correction for other titration data.

The titration data has been processed to get refined values of the formation constants using the computer program SCOGS (Stability Constants Of Generalized Species) [35-37], which employs the conventional non-linear least-squares approach. For a mixture of maximum two metals A, B and two ligands S, T, association constants may in principle be calculated with the program for any species j which can be described by the general formula.

$$A_{A_j} \; B_{B_j} \; S_{S_j} \; T_{T_j} \; (OH)_{W_j}$$

Where A_j , B_j , S_j , T_j are positive integers , or zero , and W_j is a positive integer (for a hydrolyzed species) , zero , or a nagative integer (for a protonated species). The calculated practical overall formation constant β_j can be given by the expression

$$\beta_j = \frac{[\, A_{A_j} \; B_{B_j} \; S_{S_j} \; T_{T_j} \; (OH)_{W_j} \,]}{[A]^{A_j} \; [B]^{B_j} \; [S]^{S_j} \; [T]^{T_j} \; \{OH\}^{W_j}}$$

Where square brackets [ ] denote concentrations , and braces { } denote activities.

While treating the titration data with SCOGS , activity coefficient has been considered to be equal to 1[38] and the value of the ionic product of water in 50% (v/v) aqueous dioxane (1.419×10^{-16})[38,39] has been used. Thus the constant β_j becomes pure-concentration constant.

Both , stepwise formation of the ternary complex , as well as simultaneous existance of all the species LH , L^- , AH^+ , A , Cu^{2+} , $[Cu\,A]^{2+}$, $[CuA_2]^{2+}$, $[CuL]^{1+}$, $[CuL_2]$, and $[CuAL]^*$ have been considered.

The results are recorded in Tables 2.2.1 and 2.2.2. pH titration curves have been presented in Fig. 2.2.1 to 2.2.12.

Table 2.2.1 : Stability contants of ternary complexes [CuAL] in aqueous dioxane (1:1 v/v) medium at $30^{o}C$, I = 0.2 M $NaClO_4$.

Ligand	pK_1^H	log K_{CuL}^{Cu}	log $\beta_{CuL_2}^{Cu}$	log $K_{CuAL.}^{CuA}$			
				A = dpa	A=N-phen	A=phen	A=bipy.
dpa	6.54	7.29	12.04				
N-phen	2.56	6.56	10.86				
L^1	8.55 (± 0.06)[a]	5.92 (± 0.08)	10.15 (± 0.1)	6.03 (± 0.07)	6.43 (± 0.04)		
L^2	7.68 (± 0.07)	5.29 (± 0.03)	9.16 (± 0.05)	4.66 (± 0.24)	5.38 (± 0.09)		
L^3	5.67 (± 0.02)	3.79 (± 0.06)	7.27 (± 0.03)	3.87 (± 0.08)	3.95 (± 0.05)		
L^4	7.66 (± 0.06)	6.23 (± 0.02)	11.32 (± 0.04)	6.22 (± 0.04)	6.47 (± 0.05)		
L^5	10.09 (± 0.04)	6.61 (± 0.03)	12.44 (± 0.03)	6.74 (± 0.11)	7.09 (± 0.07)		
L^6	10.98 (± 0.20)	7.69 (± 0.07)	14.03 (± 0.08)	6.61 (± 0.07)	8.62 (± 0.05)	8.76 (± 0.03)	9.30 (± 0.3)
L^7	10.27 (± 0.06)	6.85 (± 0.06)	12.06 (± 0.09)	6.32 (± 0.3)	7.85 (± 0.05)	8.00 (± 0.08)	8.46 (± 0.1)
L^8	10.14 (± 0.03)	7.11 (± 0.08)	12.92 (± 0.09)	7.89 (± 0.06)	8.08 (± 0.02)	8.12 (± 0.03)	8.69 (± 0.2)

Table 2.2.1 Contd.

L^9	9.78 (± 0.05)	7.07 (± 0.06)	12.73 (± 0.07)	7.32 (± 0.07)	8.50 (± 0.06)	8.08 (± 0.01)	8.96 (± 0.2)
L^{10}	9.33 (± 0.02)	5.64 (± 0.09)	10.52 (± 0.09)	5.99 (± 0.1)	6.41 (± 0.08)	6.82 (± 0.08)	6.81 (± 0.03)
L^{11}	8.55 (± 0.01)	4.54 (± 0.08)	9.09 (± 0.04)	5.40 (± 0.09)	5.54 (± 0.06)	5.72 (± 0.08)	5.72 (± 0.09)
L^{12}	8.42 (± 0.01)	5.14 (± 0.05)	9.20 (± 0.05)	5.78 (± 0.05)	5.92 (± 0.05)	5.74 (± 0.1)	5.82 (± 0.04)

(a) values in parantheses indicate standard deviation.

Table 2.2.2 · Δ log K values for the ternary complexes [CuAL]

Ligand	A = dpa	N - phen	phen	bipy
L^1	+ 0.11	+ 0.51	+ 0.75[a]	+ 0.94[a]
L^2	- 0.63	+ 0.09	+ 0.35[a]	+ 0.60[a]
L^3	+ 0.08	+ 0.16	+ 0.24[a]	+ 0.42[a]
L^4	- 0.01	+ 0.24	+ 0.62[a]	+ 0.73[a]
L^5	+ 0.13	+ 0.48	+ 0.96[a]	+ 1.14[a]
L^6	- 1.08	+ 0.93	+ 1.07	+ 1.61
L^7	- 0.53	+ 1.00	+ 1.15	+ 1.61
L^8	+ 0.77	+ 0.97	+ 1.01	+ 1.58
L^9	+ 0.25	+ 1.43	+ 1.01	+ 1.89
L^{10}	+ 0.35	+ 0.76	+ 1.18	+ 1.17
L^{11}	+ 0.86	+ 1.00	+ 1.18	+ 1.18
L^{12}	+ 0.64	+ 0.78	+ 0.60	+ 0.68

[a] Δ log K values have been taken from ref. 46.

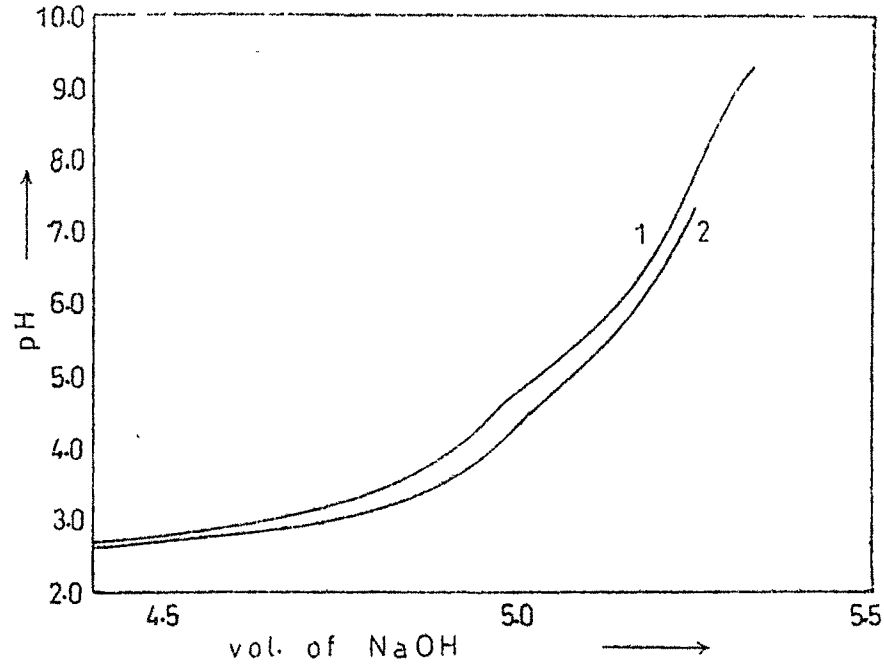

Fig. 2.2.1.

Potentiometric titration curves of 50% (v/v) aq.dioxane solutions containing metal ions , dpa or N-phen and salicylaldehyde (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + salicylaldehyde , and (2) Cu^{2+} + N-phen + salicylaldehyde.

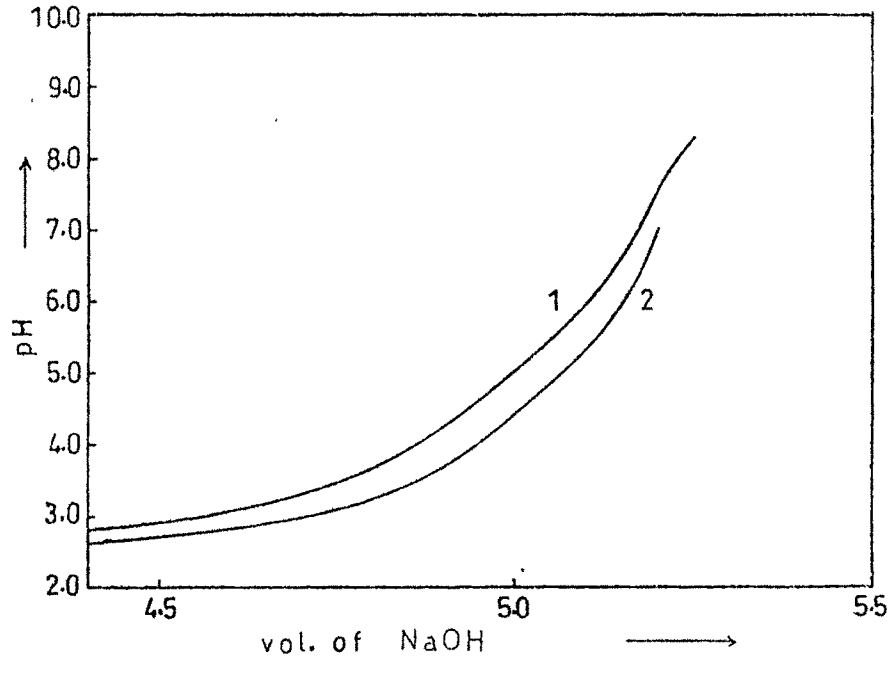

Fig. 2.2.2.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and 5-bromo salicylaldehyde (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + 5-bromo salicylaldehyde , and (2) Cu^{2+} + N-phen + 5-bromo salicylaldehyde.

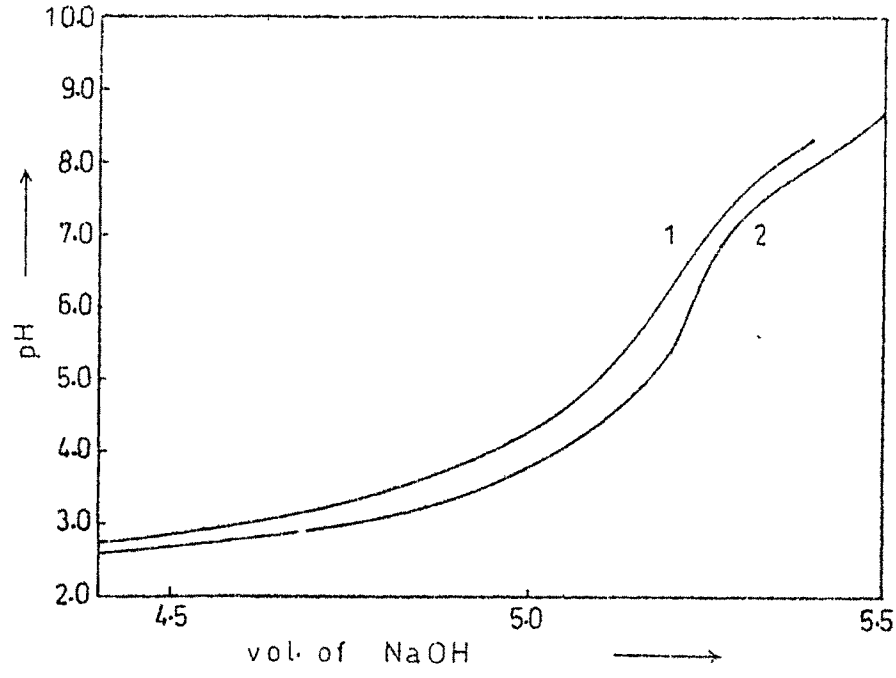

Fig. 2.2.3.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and 5-nitro salicylaldehyde (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + 5-nitro salicylaldehyde , and (2) Cu^{2+} + N-phen + 5-nitro salicylaldehyde.

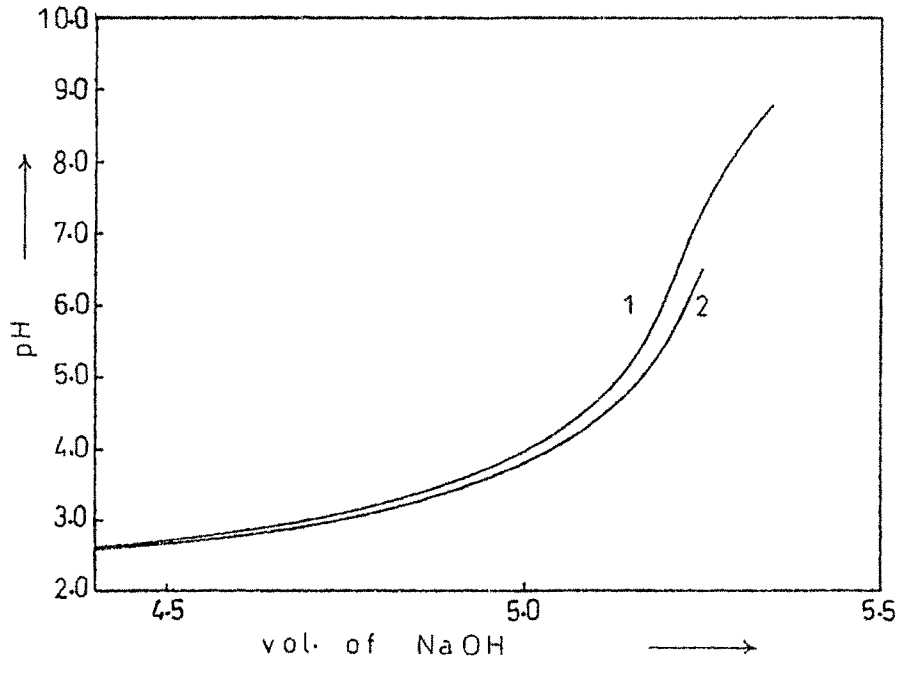

Fig. 2.2.4.

Potentiometric titration curves of 50%,(v/v) aq. dioxane solution containing metal ions , dpa or N-phen and 2-hydroxy naphthaldehyde (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + 2-hydroxy naphthaldehyde , and (2) Cu^{2+} + N-phen + 2-hydroxy naphthaldehyde.

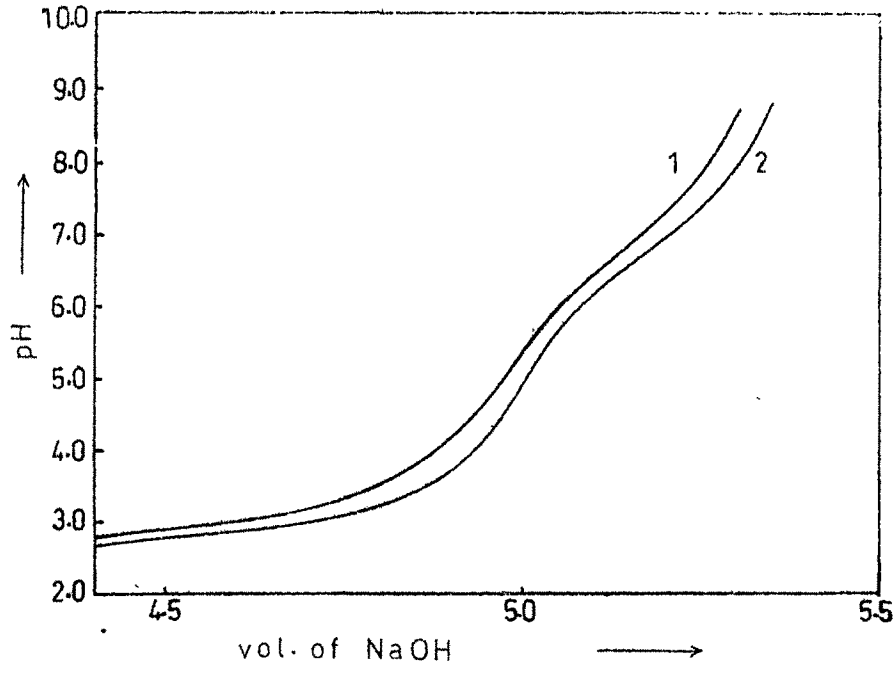

Fig. 2.2.5.

Potentiometic titration curves of 50% (v/v) aq.dioxane solutions containing metal ions , dpa or N-phen and 2-hydroxy acetophenone (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + 2-hydroxy acetophenone , and (2) Cu^{2+} + N-phen + 2-hydroxy acetophenone.

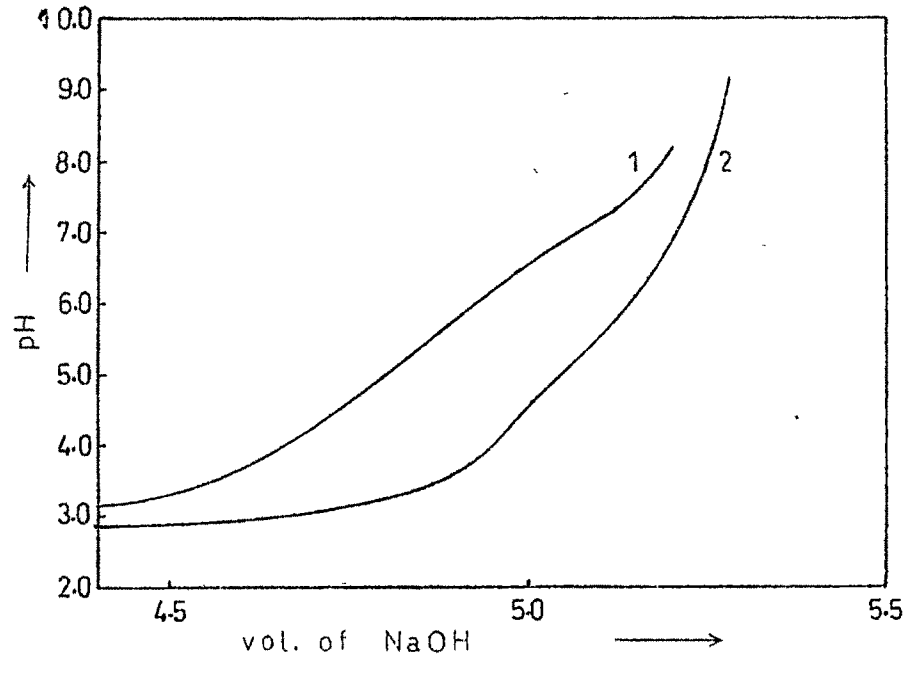

Fig. 2.2.6.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and acetoacetanilide (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} dpa + acetoacetanilide , and (2) Cu^{2+} + N-phen + acetoacetanilide.

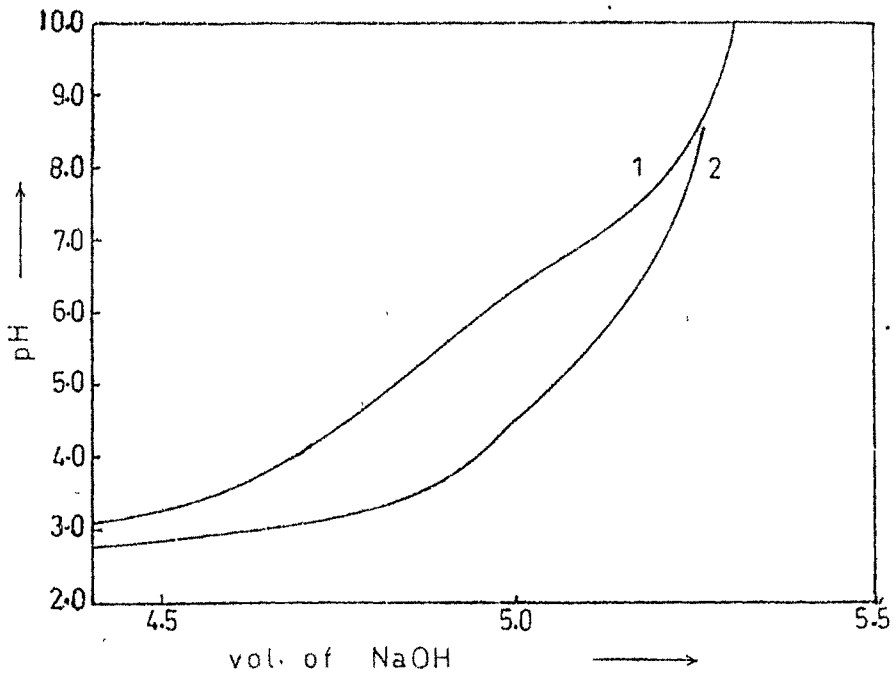

Fig. 2.2.7.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and acetoacet-o-toluedide (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + acetoacet-o-toluedide , and (2) Cu^{2+} + N-phen + acetoacet-o-toluedide.

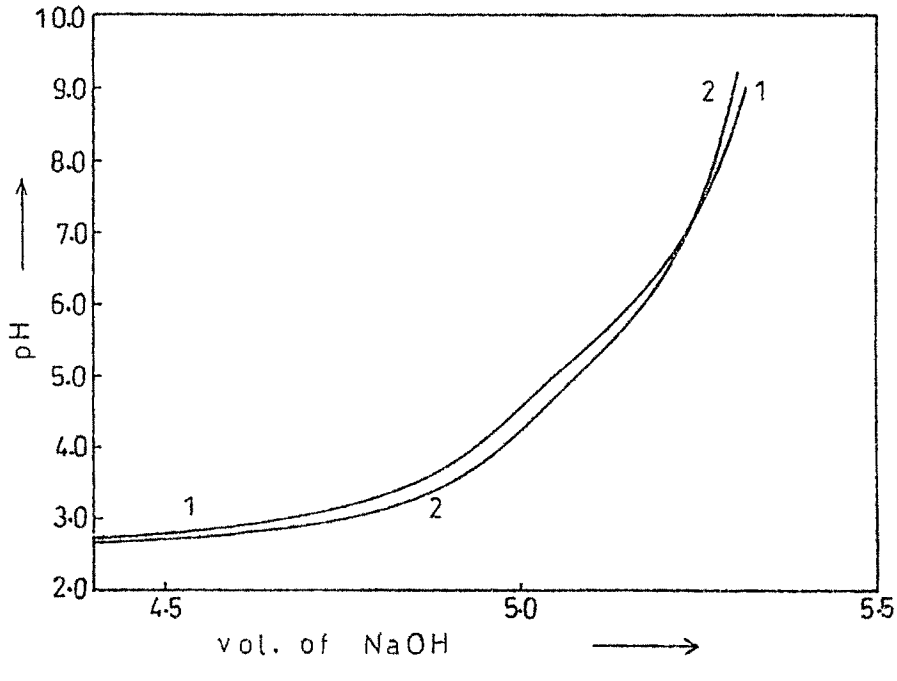

Fig. 2.2.8.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and acetoacet-o-anisidide (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + acetoacet-o-anisidide , and (2) Cu^{2+} + N-phen + acetoacet-o-anisidide.

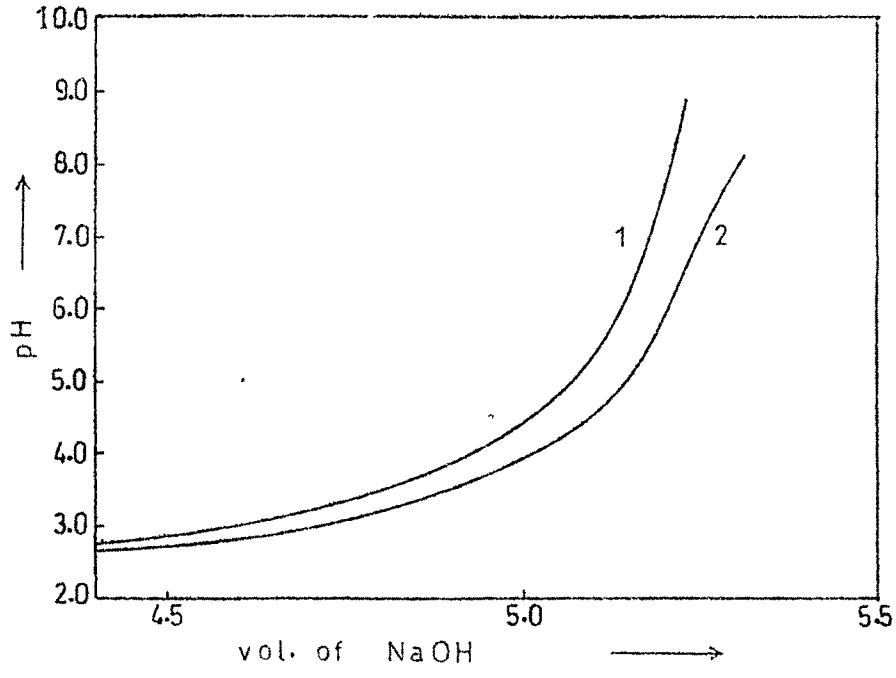

Fig. 2.2.9.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and benzoyl acetanilide (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + benzoyl acetanilide , and (2) Cu^{2+} + N-phen + benzoyl acetanilide.

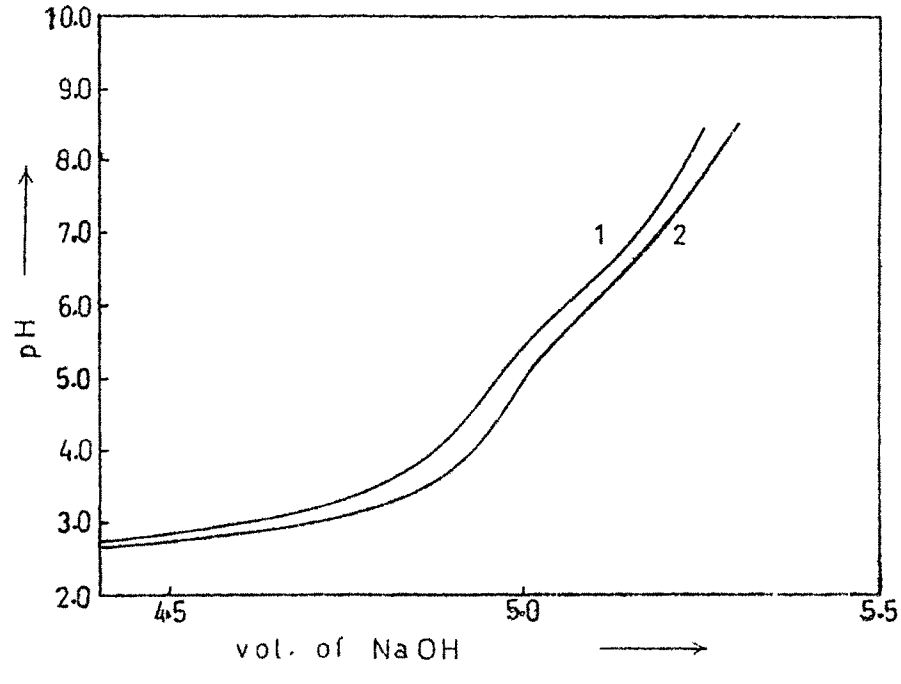

Fig. 2.2.10.

Potentiometric titration curves of 50% (v/V0 aq. dioxane solutions containing metal ions , dpa or N-phen and salicylamide (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + salicylamide , and (2) Cu^{2+} + N-phen + salicylamide.

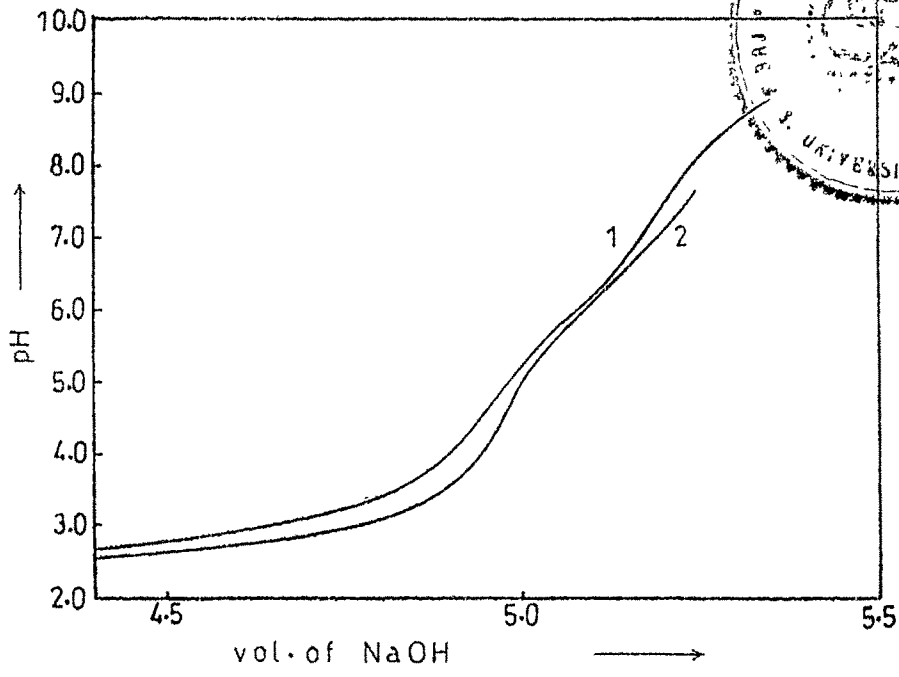

Fig. 2.2.11.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and salicyl anilide (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + salicyl anilide , and (2) Cu^{2+} + N-phen + salicyl anilide.

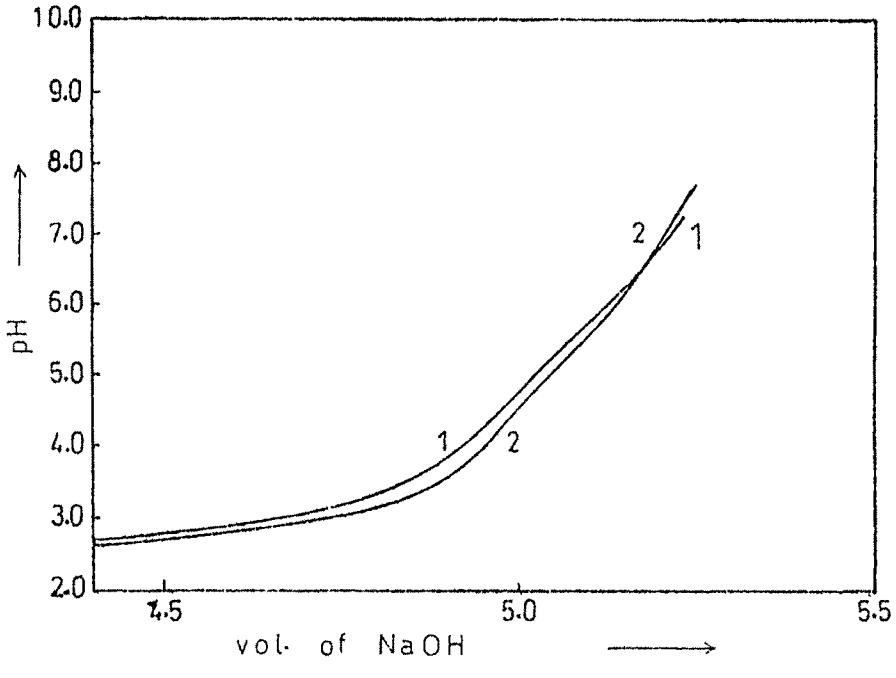

Fig. 2.2.12.

Potentiometric titration curves of 50% (v/v) aq. dioxane solutions containing metal ions , dpa or N-phen and 5-bromo salicylamide (each 1.0 x 10^{-3} M). Curve (1) Cu^{2+} + dpa + 5-bromo salicylamide , and (2) Cu^{2+} + N-phen + 5-bromo salicylamide.

2.3 Results and Discussion. [*1]

Formation of the ternary complexes in solution can be considered in two ways. The metal can combine with the primary ligand A at lower pH and then the secondary ligand starts combining with MA leading to the formation of a ternary complex. The two steps involved can be expressed as $Cu + A \rightarrow CuA$ and $CuA + L \rightleftharpoons CuAL$. Another way is to consider the pH dependant equilibrium between all the species that can be formed as a result of various reactions between the metal and the two ligands. Close agreement between the values $\log K^{MA}_{MAL}$ determined by considering the stepwise formation of the complex and the values $\log \beta^{M}_{MAL} - \log K^{M}_{MA}$ ($= \log K^{MA}_{MAL}$) determined by considering simultaneous existance of all the species [*2] , AH^{+} , A , [LH], L^{-} , $[Cu^{2+}]$, $[CuA]^{2+}$, $[CuA_2]^{2+}$, $[CuL]^{1+}$, $[CuL_2]$ and $[CuAL]^{+}$, indicates that the complex formation takes place in steps. This is also evident from the species distribution (plot of concentration of the various species) as a function of pH (Fig. 2.3.1 to 2.3.24).

As indicated by the protonation constants , the β-ketoanilides are more basic than β-diketones. However, they from less stable binary complexes with copper. In order to explain the difference in the stabilities of the binary complexes of β-diketones and β-ketoanilides , one has to consider the nature of bonding of these ligands with the central metal ion. Catechol like ligands which coordinate

[*1] Please , refer Appendix I for the description of the terms used in the following discussion.

[*2] Here onwards in the text charges on the species are omitted for clarity.

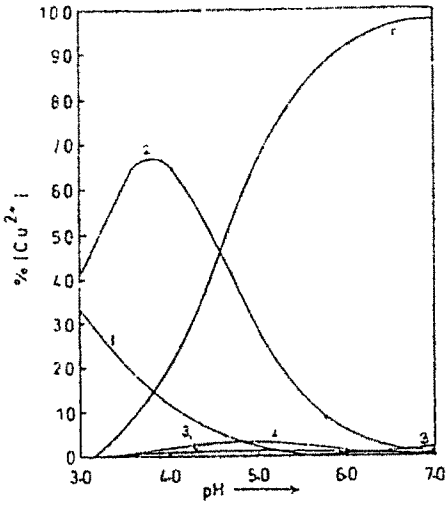

Fig. 2.3.1

Species distribution as a function of pH in the solution containing Cu , A^1 and L^1 in 1:1·1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M , 0.2.M [$NaClO_4$]. Concentration of [CuL_2] is less than 1%. Curve (1) free metal ion , (2) [CuA] , (3) [CuA_2], (4) [CuL] , and (5) [CuAL].

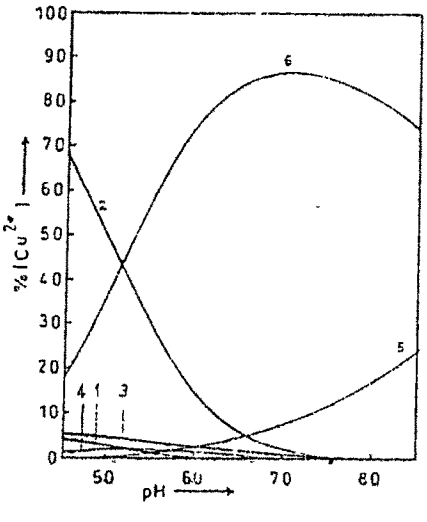

Fig. 2.3.2

Species distribution as a function of pH in the solution containing Cu , A^2 and L^1 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M , 0.2 M [$NaClO_4$]. Curve (1) free metal ion , (2) [CuA] , (3) [CuA_2], (4) [CuL] , (5) [CuL_2] and (6) [CuAL].

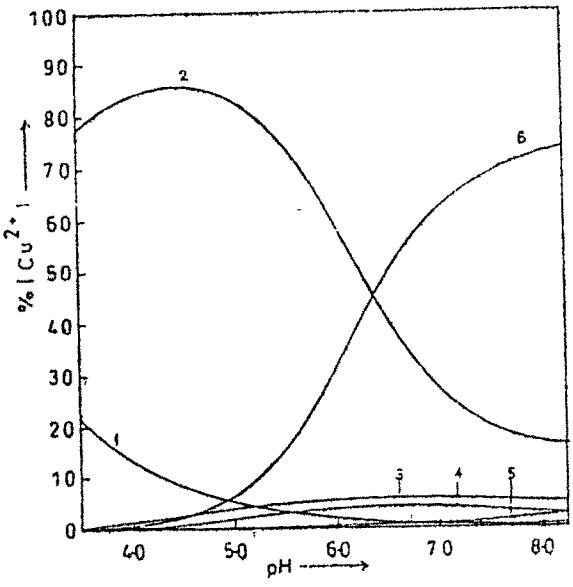

Fig. 2.3.3.

Species distribution as a function of pH in the solution containing Cu , A^1 and L^2 in 1 1 1 ratio , initial concentration of Cu^{2+} = 1.0 x 10^{-3}M , 0.2 M [$NaClO_4$]. Curve (1) free metal ion , (2) [CuA] , (3) [CuA_2], (4) [CuL] , (5) [CuL_2] and (6) [CuAL].

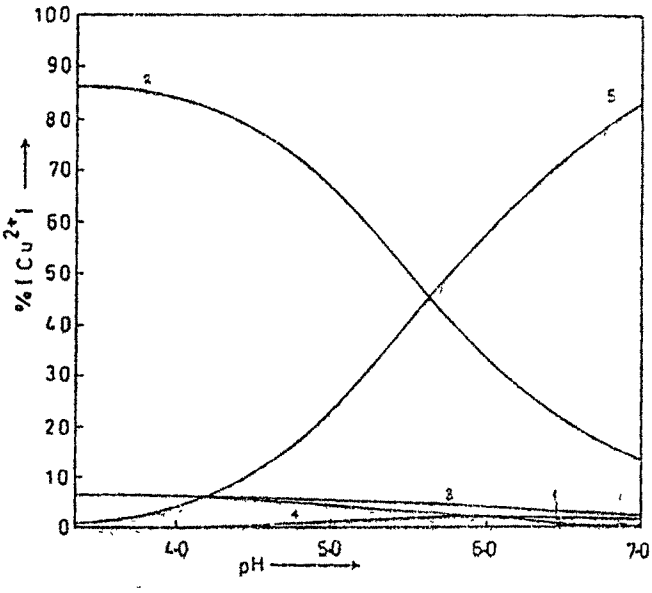

Fig. 2.3.4.

Species distribution as a function of pH in the solution containing Cu , A^2 and L^2 in 1:1·1 ratio , initial concentration of Cu^{2+} = 1.0 x 10^{-3}M , 0.2.M [$NaClO_4$]. Concentration of [CuL_2] is less than 1%. Curve (1) free metal ion , (2) [CuA] , (3) [CuA_2], (4) [CuL] , and (5) [CuAL].

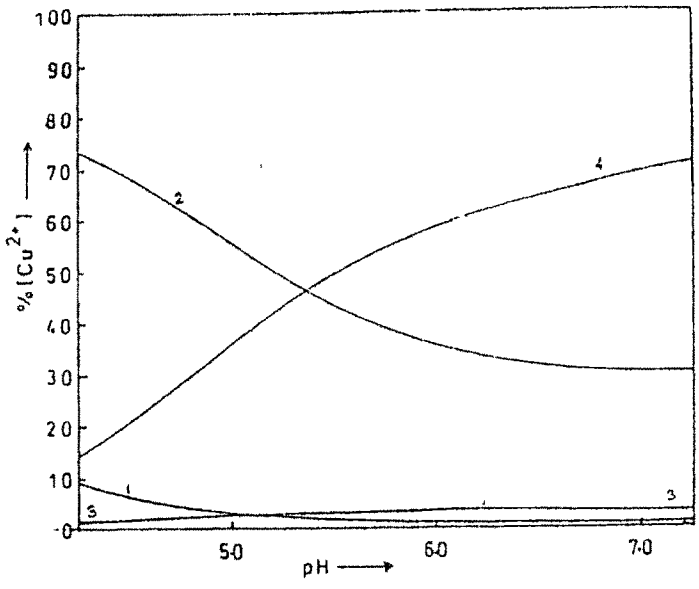

Fig. 2.3.5.

Species distribution as a function of pH in the solution containing Cu , A^1 and L^3 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0×10^{-3}M, 0.2 M [$NaClO_4$] Concentrations of [CuL_1] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA] , (3) [CuA_2] and (4) [CuAL].

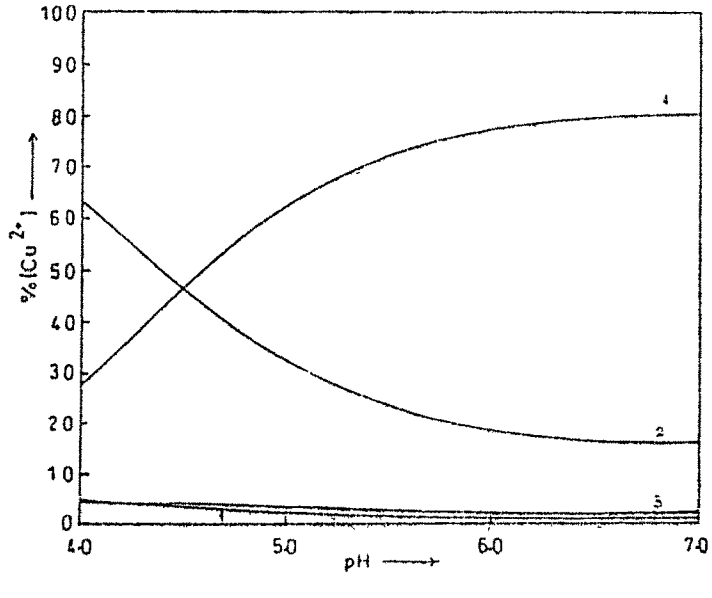

Fig. 2.3.6

Species distribution as a function of pH in the solution containing Cu , A^2 and L^3 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0×10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA] , (3) [CuA_2] and (4) [CuAL].

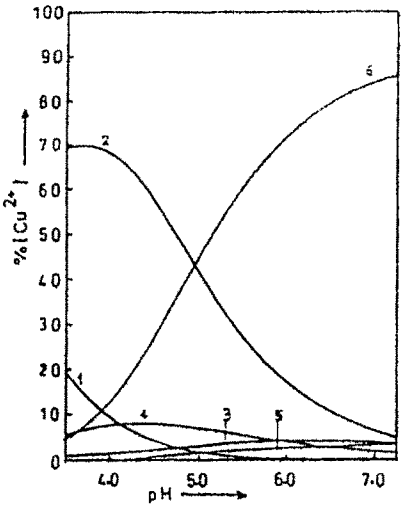

Fig. 2.3.7

Species distribution as a function of pH in the solution containing Cu , A^1 and L^4 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0×10^{-3}M , 0.2 M [$NaClO_4$]. Curve (1) free metal ion , (2) [CuA], (3) [CuA_2], (4) [CuL] , (5) [CuL_2] and (6) [CuAL].

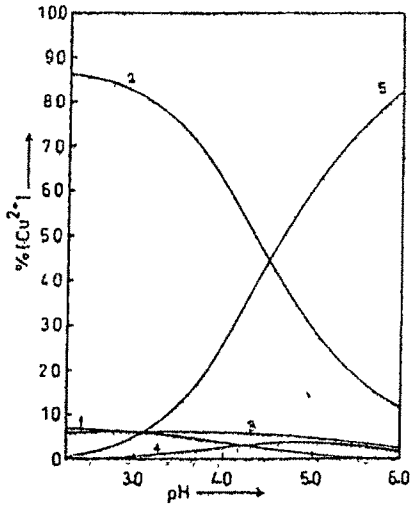

Fig. 2.3.8

Species distribution as a function of pH in the solution containing Cu , A^2 and L^4 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0×10^{-3}M , 0.2.M [$NaClO_4$]. Concentration of [CuL_2] is less than 1%. Curve (1) free metal ion , (2) [CuA] , (3) [CuA_2], (4) [CuL] , and (5) [CuAL].

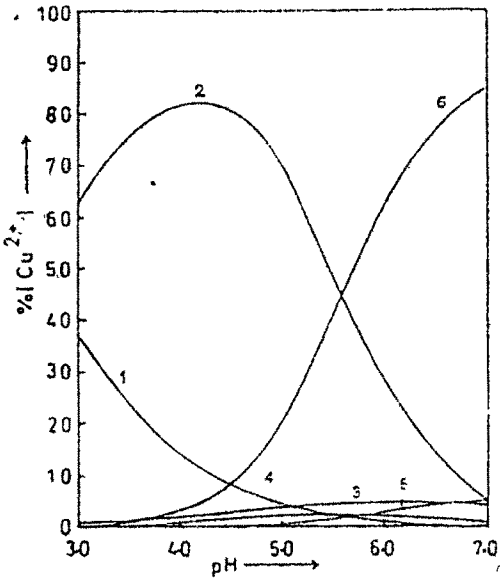

Fig. 2.3.9

Species distribution as a function of pH in the solution containing Cu , A^1 and L^5 in 1:1:1 ratio , initial concentration of Cu^{2+} = 1.0×10^{-3}M , 0.2 M [$NaClO_4$]. Curve (1) free metal ion , (2) [CuA] , (3) [CuA_2], (4) [CuL] , (5) [CuL_2] and (6) [CuAL].

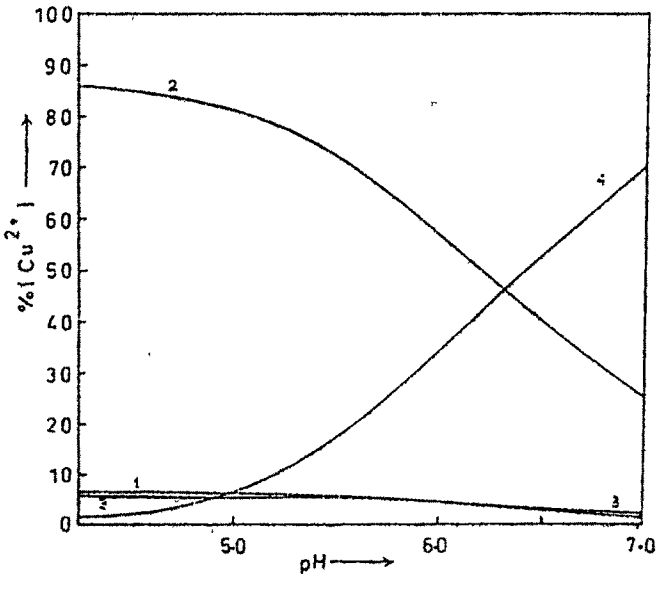

Fig. 2.3.10

Species distribution as a function of pH in the solution containing Cu , A^2 and L^5 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0×10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%. Curve (1) free metal ion, (2) [CuA] , (3) [CuA_2] and (4) [CuAL].

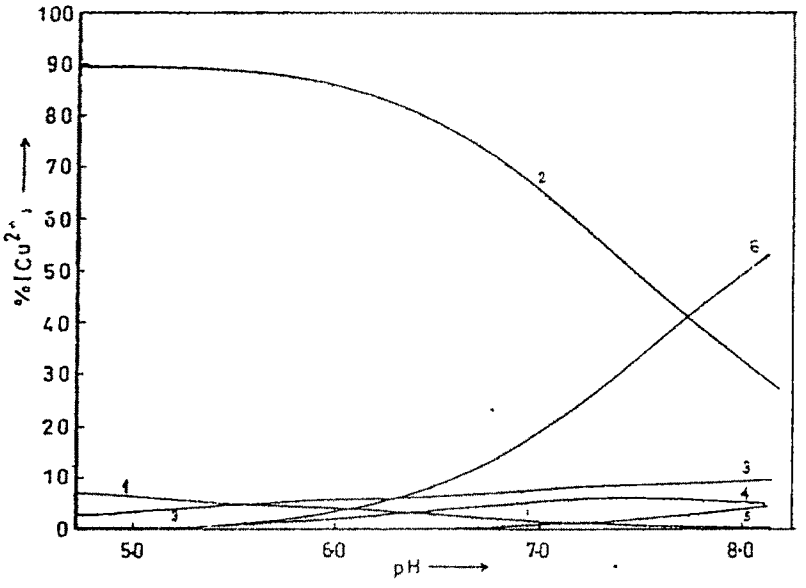

Fig. 2.3.11

Species distribution as a function of pH in the solution containing Cu , A^1 and L^6 in 1:1:1 ratio , initial concentration of Cu^{2+} = 1.0 x 10^{-3}M , 0.2 M [$NaClO_4$]. Curve (1) free metal ion , (2) [CuA], (3) [CuA_2], (4) [CuL] , (5) [CuL_2] and (6) [CuAL].

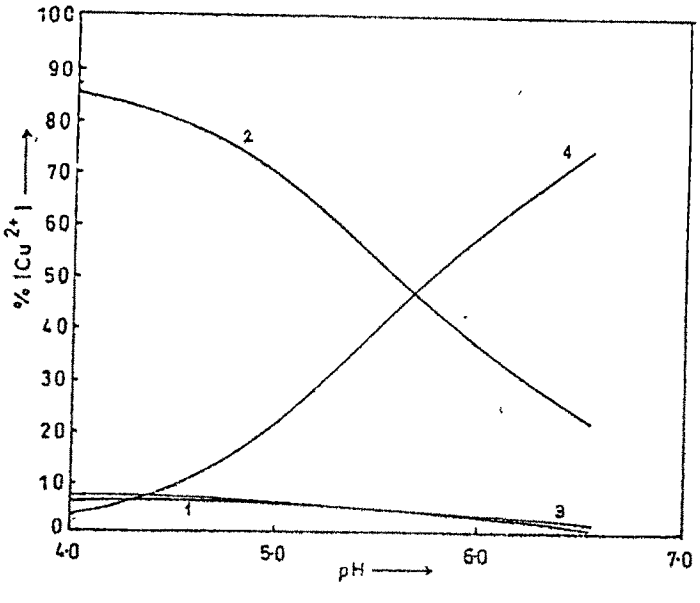

Fig. 2.3.12

Species distribution as a function of pH in the solution containing Cu , A^2 and L^6 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%. Curve (1) free metal ion, (2) [CuA] , (3) [CuA_2] and (4) [CuAL].

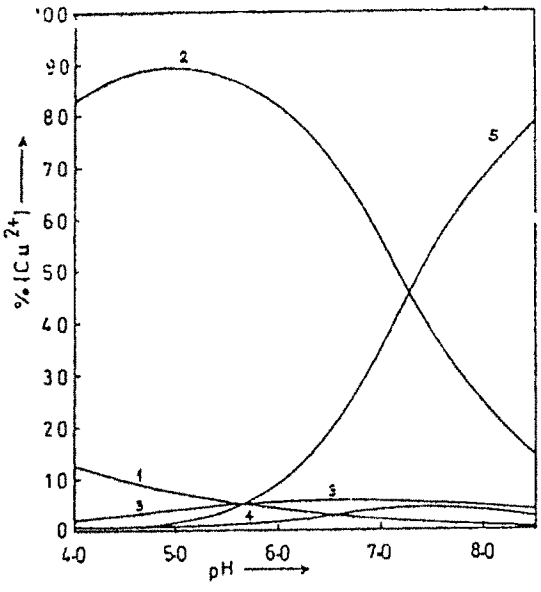

Fig. 2.3.13

Species distribution as a function of pH in the solution containing Cu , A^1 and L^7 in 1:1:1 ratio , initial concentration of Cu^{2+} = 1.0 x 10^{-3}M , 0.2.M [$NaClO_4$]. Concentration of [CuL_2] is less than 1%. Curve (1) free metal ion , (2) [CuA] , (3) [CuA_2], (4) [CuL] , and (5) [CuAL].

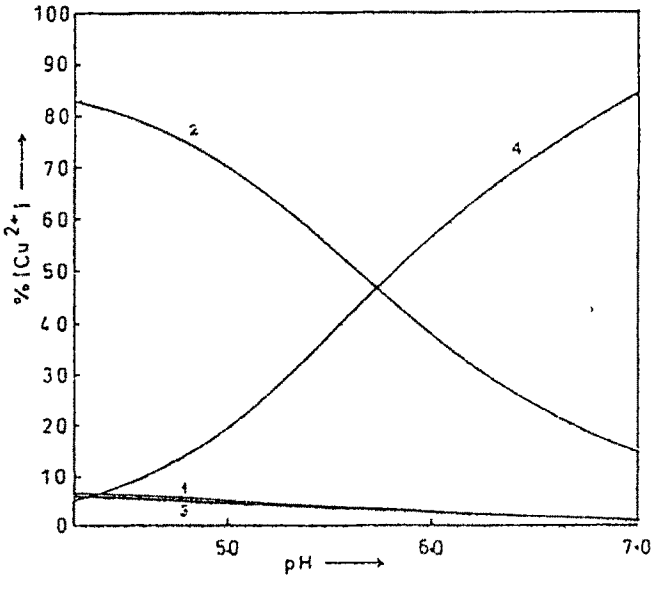

Fig. 2.3.14

Species distribution as a function of pH in the solution containing Cu , A^2 and L^7 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA] , (3) [CuA_2] and (4) [CuAL].

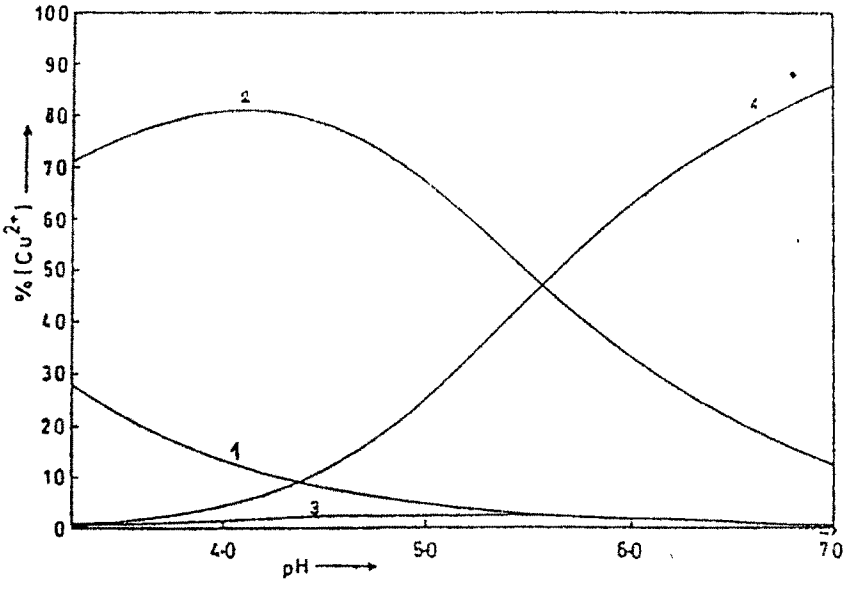

Fig. 2.3.15

Species distribution as a function of pH in the solution containing Cu , A^1 and L^8 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3) [CuA_2] and (4) [CuAL].

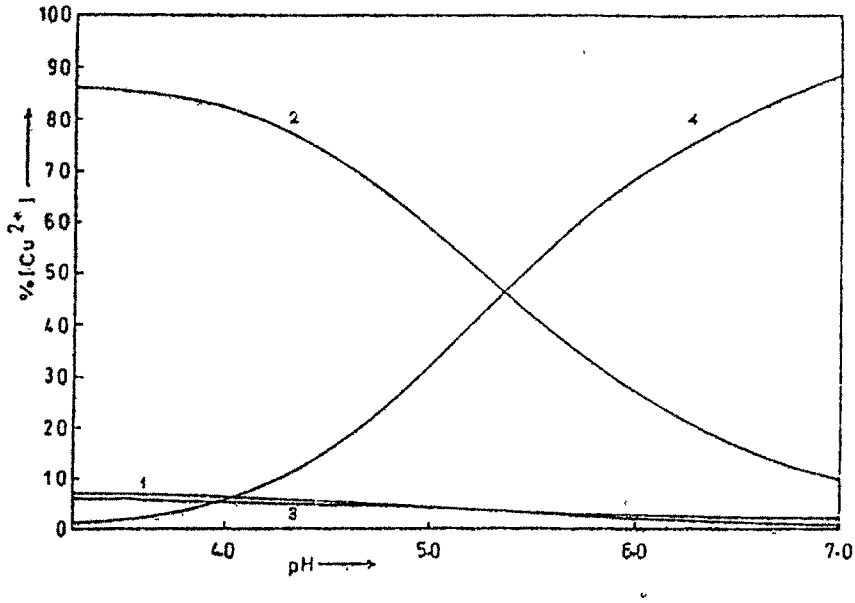

Fig. 2.3.16

Species distribution as a function of pH in the solution containing Cu , A^2 and L^8 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3) [CuA_2] and (4) [CuAL].

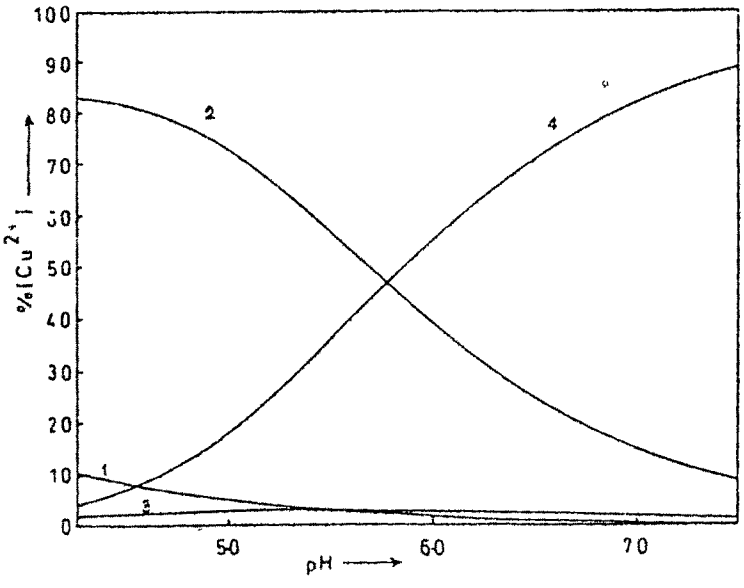

Fig. 2.3.17

Species distribution as a function of pH in the solution containing Cu , A^1 and L^9 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3) [CuA_2] and (4) [CuAL].

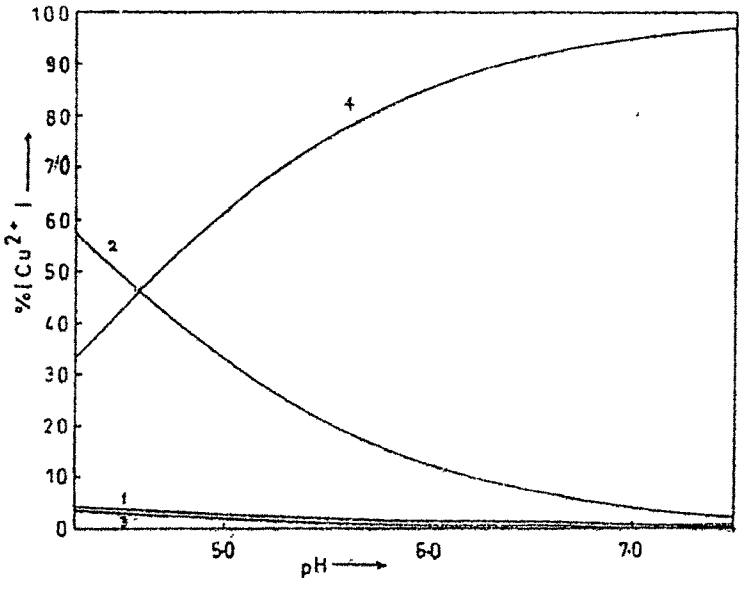

Fig. 2.3.18

Species distribution as a function of pH in the solution containing Cu , A^2 and L^9 in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3) [CuA_2] and (4) [CuAL].

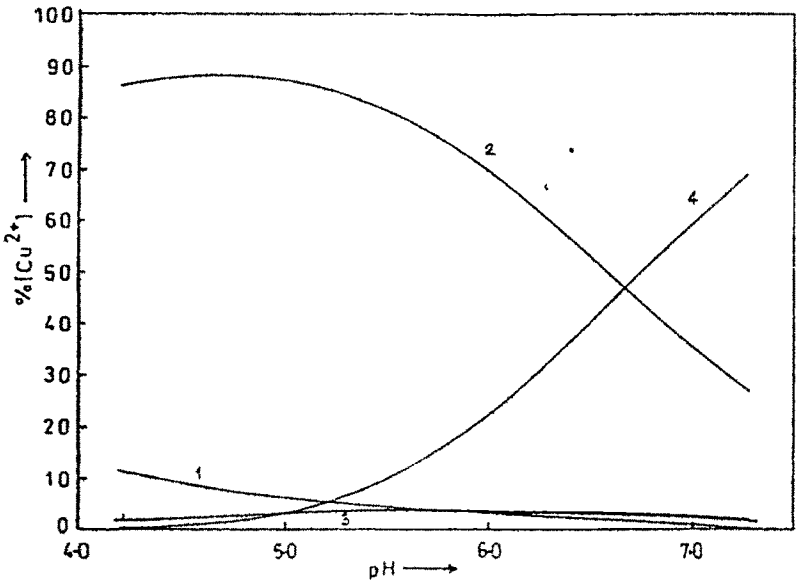

Fig. 2.3.19

Species distribution as a function of pH in the solution containing Cu , A^1 and L^{10} in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 .x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3)[CuA_2] and (4) [CuAL].

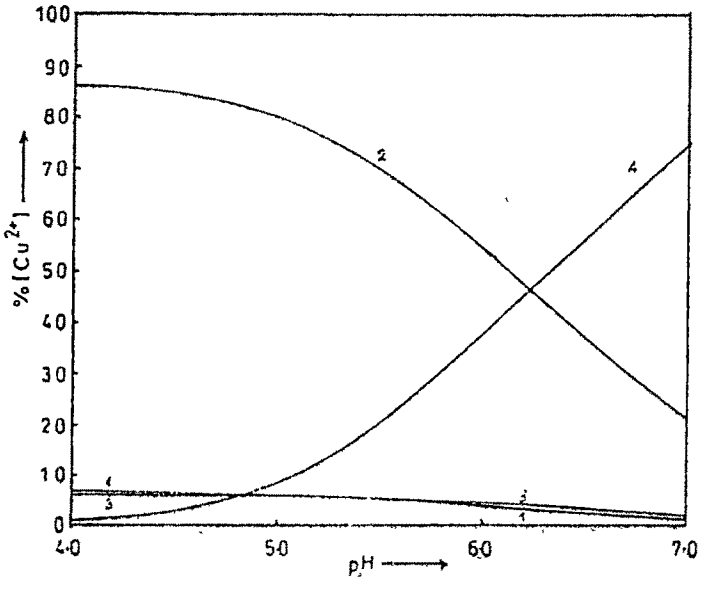

Fig. 2.3.20

Species distribution as a function of pH in the solution containing Cu , A^2 and L^{10} in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3)[CuA_2] and (4) [CuAL].

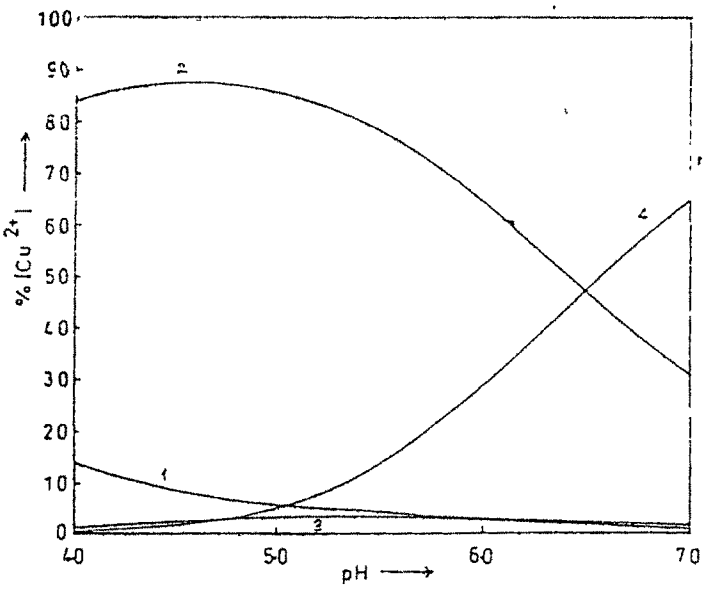

Fig. 2.3.21

Species distribution as a function of pH in the solution containing Cu , A^1 and L^{11} in 1 1 1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3) [CuA_2] and (4) [$CuAL$].

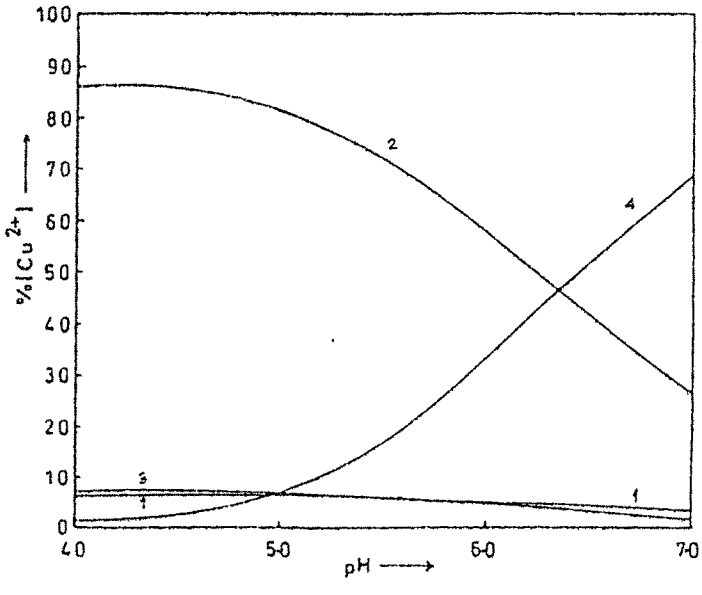

Fig. 2.3.22

Species distribution as a function of pH , in the solution containing Cu , A^1 and L^{11} in 1 1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA], (3) [CuA_2] and (4) [$CuAL$].

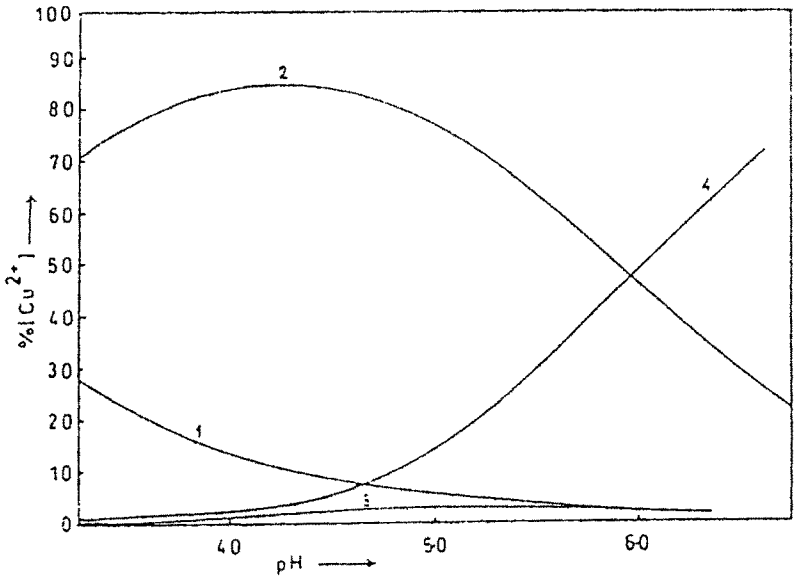

Fig. 2.3.23

Species distribution as a function of pH in the solution containing Cu , A^1 and L^{12} in 1:1:1 ratio ; initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA] , (3)[CuA_2] and (4) [CuAL].

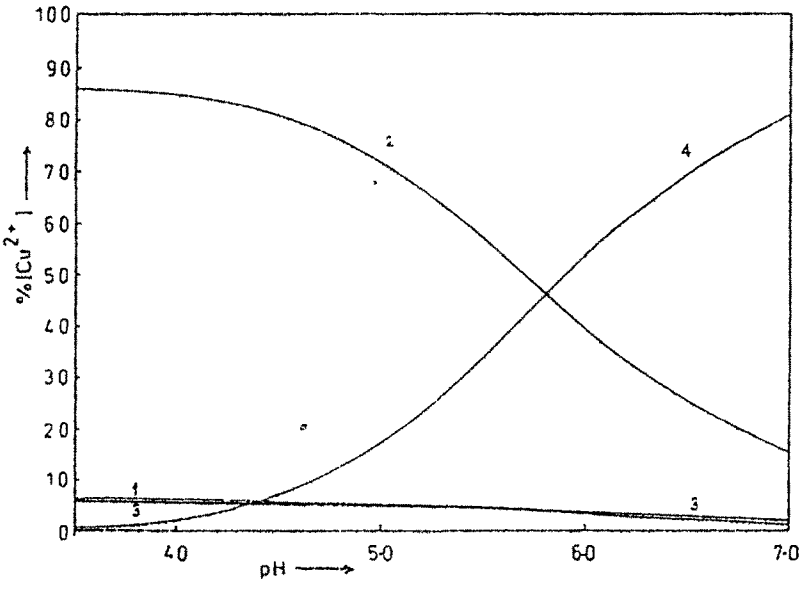

Fig. 2.3.24

Species distribution as a function of pH in the solution containing Cu , A^2 and L^{12} in 1:1:1 ratio , initial concentration of Cu^{2+} = 1.0 x 10^{-3}M, 0.2 M [$NaClO_4$]. Concentrations of [CuL] and [CuL_2] are less than 1%.Curve (1) free metal ion, (2) [CuA] , (3)[CuA_2] and (4) [CuAL].

through strong electron donating O^- - O^- sites form strong σ bonds with the metal ion. The σ basicity of the coordinating ligands like β-diketones with one O^- replaced by weak donor carbonyl oxygen is less than O^- - O^- coordinating ligands. However, these ligands have vacant π orbitals to accept electrons from the metal and the resulting complex has pseudoaromatic character[40-43], which, in effect, stabilizes the complex. β-ketoanilides or salicylaldehyde like ligands have O^- - O coordinating sites with less basicity than O^- - O^-, and carbonyl oxygen with π orbitals. Although, the presence of π orbitals over the coordinating atom makes M $\rightarrow$ L π bonding possible, the delocalization of π electron density over the whole chelate ring requires the contribution of a less stable resonance form, in which aromaticity of the phenyl ring in salicylaldehyde is destroyed. In β-ketoanilides ^+N ------ C ----- O^- resonance form (mesomeric electron release by amide N) makes the amide O less susceptible to accept electrons from the metal ion and hinders the delocalization of π electrons over the chelate ring. Thus the two classes of ligands, β- ketoanilides and salicylaldehydes, are borderline cases between σ bonding ligands, like catechol with O^- - O^- coordinating sites and O^- - O ligands like β-diketones which have extensive π bonding. Only slight tendency of the earlier ligands to undergo π interaction with the metal ion make them behave, preferentially, as σ bonding ligands. In most cases the fine tuning between both the σ and π bonding characteristics of the ligands in ternary complexes can get adjusted according to the characteristics of the other ligand and attain the most stable state of energy.

Stability of the ternary complexes :

Formation constant values in Table 2.2.1 reveal that the ternary complexes of copper (II) with tertiary diimines as primary ligand and O^- - O coordinating secondary ligand are more stable than the corresponding binary complexes of the

ligands resulting in more positive Δ log K than the values expected on the basis of the statistical consideration (Appendix 1). In the binary complexes of the ligands with O^- - O sites, the ligand electrons have to face repulsion from the metal d_π electrons thus resulting in less stable binary complex. However, in the ternary complex the electron density over the metal gets reduced due to M → A π interaction and hence the ligand L realizes less repulsion while combining with [MA] than with free metal ion. Thus the release of repulsion in the ternary complex results in the greater stabilization and less negative Δ log K value.

Substitution on primary ligands :

Similar explanantions can be extended for the order of Δ log K observed with various combinations of primary and secondary ligands. Apparently, increase in π acidity of the primary ligand should lower down the electron density over the metal ion to a greater extent and hence electron withdrawing substituent on A should result in greater stabilization of the ternary complexes. However, the order of stabilization in the ternary complexes of salicylaldehyde derivatives and β-ketoanilides is observed to be quite reverse. According to Tabel 2.2.2 the Δ log K values of the complexes follow, more or less the following order. [Cu dpa L] < [Cu bipy L] > [Cu phen L] > [Cu N-phen L] . 1,10-phenanthroline which has greater π delocalization than 2,2'-bipyridyl acts as a stronger π acid. Electron withdrawing - $-NO_2$ group in 5-nitro-1,10-phenanthroline pulls the electron density from the coordinating sites and hence makes it a stronger π acid than 1,10-phenanthroline. i.e. the π acid character increases in the order bipy < phen < N-phen and the stability of the ternary complexes follows the reverse order. This may be because greater withdrawl of electron density by A from the metal ion makes it more of class A character which demands a

second ligand with strong σ basic sites for coordination. The O^- - O ligands like salicylaldehyde or β-ketoanilides may not be able to provide such stronger sites. Hence, complexes of the type [Cu A salicylaldehydate or [Cu A β-ketoanilide] having electron withdrawing substituents like - NO_2 group on A and hence greater Cu → A π interaction, will be less stable. Further, [Cu dpa L] complexes which have two six membered chelate rings are less stable than [Cu bipy L] having one five membered and one six membered chelate ring [44,45] .

Substitution on O^- - O coordinating ligands :

It is also interesting to observe the effect of the nature of substitution over the secondary ligand on the formation constants of the ternary complexes. Comparison within the series of complexes with 2-hydroxy aromatic carbonyls (Table 2.2.2) indicates that Δ log K value is less positive for [Cu A L] $^+$ complexes where HL = 5-bromo or 5-nitrosalicylaldehyde than the respective [Cu A salicylaldehydate] $^+$ complexes. This is also true for [Cu A 2-hydroxy naphthaldehydate] $^+$ complexes where a phenyl ring is fused in the 5-6 position. This is because of the electron withdrawing effect of the nitro-and bromo- groups or the fused phenyl ring. Complexes of [Cu A] $^{2+}$ with 2-hydroxy aceto-phenone, having an electron releasing methyl group as a substituent at carbonyl carbon, are expected to be slightly more stable than their salicylaldehyde analogues due to the electron releasing effect of the $-CH_3$ group. However, in the present study we found Δ log K for [Cu A salicylaldehydate] $^+$ and [Cu A 2-hydroxy acetophenonate] $^+$ to be very close, probably because of the small electron releasing tendency of the - CH_3 group. These observations are in

agreement with earlier results[46]. This can be explained on the basis of the electron repulsion concept. When a ligand coordinates with the metal ion through O^-, there is Coulombic repulsion between the metal $d\pi$ electrons and the extra lone pair of electrons on O^-. Coordination with a π bonding ligand like tertiary diimine (A) decreases the π - electron density over the metal ion through metal-to-ligand π bonding. When a secondary ligand with O^- - O coordinating sites binds with $[MA]^{n+}$, it realizes less repulsion from the metal $d\pi$ electrons than when it binds with the free metal ion. This results in greater stability of the ternary complex compared to the corresponding binary complex. Substitution over the secondary ligand will affect the electron density over the coordinating atom and hence stability of the complex. Observations made in the present study are in accordance with the expectation that the electron withdrawing group lowers the negative charge density over O^-- O whereas an electron-releasing - CH_3 group increases the electron density, resulting in destabilization or stabilization, respectively, of the ternary complexes.

Similar trend has been observed in the order of stabilization of the ternary complexes containing β-ketoanilides as secondary ligands. The electron releasing substituents on the anilide rings of the secondary ligands increase the basicity of the amide N and hence increase the σ basicity and decrease the π bonding ability of the amide oxygen. This results in less stable binary and more stable ternary complexes and hence more positive Δ log K values. However, the phenyl substituent in benzoyl acetanilide although being electron withdrawing does not destabilize the complex. This is because, the phenyl group (of the benzoyl part) decreases the basicity of O^- without compensating the electron release and hindered π electron delocalization by amide N and hence lowers the stability of the binary complex.

As far as salicylamide is concerned, it fits well in the order of stabilities of the complexes of other salicylaldehyde derivatives, i.e. Δ log K for [Cu A salicylamide] is more positive than that of the corresponding salicylaldehyde containing ternary complex. However, the complexes of salicylamide ligands are rather insensitive to the substitution over the primary ligand. The Δlog K for the complexes with different primary ligands are almost similar within the uncertainity range of the values. In these ligands the phenyl ring can not contribute to the π delocalization in the chelate ring without disturbing its own aromaticity. This is combined with amide N having mesomeric electron releasing effect which makes >C=O difficult to accept electrons from the metal. The two, in effect, destroy the π bonding ability of these ligands in their complexes.

Electronic spectra and stability of the complexes :

Energy of the electronic transitions between the metal d orbitals correspond to the crystal field stabilization and hence is expected to be related with the stability of the complexes. The positions of the ligand field transitions ($\bar{\nu}_c$) observed in the solutions of the ternary complexes (Chapter 3) in 50% (v/v) aqueous dioxane have been recorded in Table 2.3.1. If we consider the $\bar{\nu}$(d-d) in binary complexes [Cu A_2] and [Cu L_2] of primary and secondary lgands to be $\bar{\nu}_1$ and $\bar{\nu}_2$, respectively, the difference between observed $\bar{\nu}_c$ and the value of the energy of the d-d transition estimated from the average of $\bar{\nu}_1$ and $\bar{\nu}_2$ will be a measure of extra stabilization or destabilization of the ternary complex.

$$\Delta \bar{\nu} = \bar{\nu}_c - (\bar{\nu}_1 + \bar{\nu}_2)/2$$

It is observed that $\Delta\bar{\nu}$ (Table 2.3.1) has a positive value indicating that the ternary complex is more stabilized than expected from the average field created by the two ligands. This supports mutual effect of the two ligands in

stabilizing the metal-ligand interaction. π interaction between the vacant π orbitals of one ligand and the filled metal d_π orbitals results in stronger σ bond formation between metal and the second ligand i.e. the σ antibonding orbitals are elevated in energy. At the same time stronger M-L σ bonding increases the electron density over the metal ion which favours a stronger π interaction with the other ligand. This lowers down the π bonding orbitals - which are essentially metal d_π orbitals - in energy. Thus, the separation between the metal d orbitals and hence the energy of the d-d transition increases. Spectrophotometrically determined $\Delta\bar{\nu}$ and potentiometrically determined Δ log K, both are measure of the stability of the ternary complex and their order is comparable. However, there is no linear relationship. This is because $\Delta\bar{\nu}$ is related only with the crystal field created by the ligands whereas both, enthalpy and entropy, affect Δ log K values.

Table 2.3.1 : Ligand field bands of [CuAL] complexes in 50% (v/v) aq. dioxane ($\bar{\nu}$ in 10^3 cm^{-1}).

	$\bar{\nu}$ in	A = A^1				A = A^2	
L	CuL_2	$\bar{\nu}_a$	$\bar{\nu}_b$	$\Delta\bar{\nu}$ (a)	$\bar{\nu}_a$	$\bar{\nu}_b$	$\Delta\bar{\nu}$
A^1	15.20						
A^2	14.28						
L^1	12.63	15.87 (87)(b)	-	1.95	15.82 (84)	-	2.37
L^2	12.53	15.77 (88)	-	1.90	15.75 (103)	-	2.34
L^3	12.66	15.67 (86)	-	1.74	15.70 (89)	-	2.23
L^4	13.11	16.45 (114)	-	2.29	16.29 (96)	-	2.59
L^5	12.45	16.08 (96)	-	2.26	15.87 (169)	18.11 (179)	2.505
L^6	15.34	16.03 (69)	25.19 (210)	0.76	15.75 (51)	19.61 (42)	0.94
L^7	15.38	15.97 (59)	25.38 (190)	0.68	15.92 (61)	19.61 (53)	1.09
L^8	15.20	16.00 (68)	25.32 (220)	0.8	15.95 (61)	19.68 (62)	1.21
L^9	15.27(c)	16.05 (70)	21.74 (156)	0.81	15.62 (53)	21.74 (69)	0.85

Table 2.3.1 Contd.

L^{10}	14.75	15.75 (83)	25.0 (335)	0.77	15.65 (82)	23.81 (373)	1.13
L^{11}	14.79	15.67 (85)	23.53 (371)	0.68	15.48 (81)	23.53 (365)	0.94
L^{12}	14.97	15.62 (96)	23.81 (397)	0.54	15.55 (88)	23.81 (465)	0.92

(a) $\bar{\nu}_a$ values have been used for the calculation of $\Delta\bar{\nu}$

(b) Molar absorbance values are given in parentheses,

(c) $\bar{\nu}$ in methanol.

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