ligand combines with metal ions, attachment of secondary ligand does not take place. The mixed complex curve separates from primary complex curve at pH 2.0 due to the self dissociation of the secondary ligands After pH 4.0, mixed complex curve shows attachment of secondary ligand to the primary complex. In the case of ARS the complexation starts around pH 5.0 and in the case of IMDA it starts at higher pH. Since the dissociation of primary complex does not take place in the range of dissociation of secondary ligand, it can be considered that secondary ligand combines with the binary primary ligand-metal complex. In the presence of secondary ligand, formation of [M(III)-A-(OH)$\bar{n}$] is also suppressed. The $\bar{n}$ values have been calculated from the titration curves and using these $\bar{n}$ values, formation curves at 25° were constructed. The values of log K_{MAL}^{MA} have been evaluated from the formation curves using the method of interpolation at various $\bar{n}$ values and are recorded in Table 2. The error limits are of ± 0.08 log units.

The stability constants of ternary complexes, give the following order stability with change in secondary ligand : ARS > OSA > IOSA > IMDA. This trend in the stability can be attributed to the basicity of the ligand, nature of donating groups and the size of the ring formed. The affinity of rare earths for phenoxide ions as the coordinating group, explains the higher stability of ARS complexes[7]. ARS has two *ortho*-hydroxy groups whereas OSA and IOSA have only one phenoxide group.

The mixed ligand complexes of OSA are more stable than of IOSA due to the presence of electron withdrawing group which decreases the basicity of the ligand. IMDA forms less stable mixed ligand complexes with six-membered ring by coordinating through two carboxylic groups. The other ligands form five-membered ring and the complexation occurs through two or atleast one phenoxide group. The relative order of stability in terms of metal ions is Ho(III) > Gd(III) > Sm(III) > Nd(III), which may be probably due to the decreasing ionic radius and increasing charge/radius ratio of the metal ions. On the basis of experimental evidences collected in the present study, it is possible to make positive suggestions in favour of the expansion of coordination number of Nd(III), Sm(III), Gd(III) and Ho(III) from six to eight.

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Potentiometric Studies on Binuclear Metal Complexes of 1,2-Diaminocyclohexanetetraacetic Acid & Bidentate Ligands

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The pH-metric evidence for the formation of binuclear ternary species of the type M_2LA and M_2LA_2 [M = Cu(II), Ni(II) and Zn(II), L = 1,2-diaminocyclohexanetetraacetic acid (CDTA), A = ethylenediamine (en) or 1,2-propanediamine (pn)] is provided. Formation constants of the resulting ternary species at $25^\circ \pm 1^\circ$ ($\mu = 0.1$ M KNO$_3$) have also been evaluated. The insoluble binuclear 2:1:2, Cu(II)-CDTA-HQ complex (HQ=8-hydroxyquinoline) has been tested on some fungi and bacteria and has been found to be more active as compared to the free ligands and the Cu(II)-HQ complex.

EXTENSIVE studies have been made on the ternary systems involving transition metal ions, but binuclear mixed-ligand complexes have not received as much attention[1,2]. It has, therefore, been considered of interest to investigate some of the systems of the type M_2-CDTA-(diamines)$_2$[M =Cu(II), Ni(II) and Zn(II); diamines = ethylenediamine (en) or propylenediamine (pn); CDTA = 1,2-diaminocyclohexanetetraacetic acid]. The formation constants of the resulting soluble binuclear mixed ligand species have now been evaluated pH-metrically.

The insoluble binuclear mixed-ligand complex, $(Cu)_2$-CDTA-(HQ)$_2$ (where HQ = 8-hydroxyquinoline) has been isolated and its biocidal activity towards some fungi (*Penicillium chrysogenum* (Thom), *Aspergillus terrus* (Thom) and *Alternaria alternata* (Fr.) Keissler and bacteria (*Staphyllococcus* and *Streptococcus*) has been investigated.

All the chemicals used were either of AR (BDH) or GR (E. Merck) grade unless stated otherwise. Solutions of metal nitrates and diamines dihydrochlorides were prepared and standardised as described in the earlier communication[1,3]. The solutions of 8-hydroxyquinoline hydrochloride and tri-potassium salt of CDTA (CDTA being insoluble in water) were prepared by dissolving the weighed amounts of the respective substances in calculated amount of standard 0.1 M HCl and 0.1M KOH respectively. The concentration of the stock solutions was checked by the potentiometric titrations. The detailed experimental procedure has also been described earlier[1].

The acid dissociation constants of en.2H$^+$ (7.08, 9.78), pn.2H$^+$ (6.96, 9.82) and K$_3$CDTA (11.22) were calculated by the method of Chaberek and Martell[4].

The formation constants of the binuclear species were evaluated by the methods described in previous communication[1] by considering the two modes : (i) simultaneous addition of both the diamine molecules to the initially formed M_2^{2+} - CDTA species and (ii) the addition of one of the two molecules of diamines to the intermediate M_2-CDTA-en/pn species. The formation constants of the binary species (Table 1) calculated by the method of Thompson and Loraas[5] were obtained for comparison.

The set of curves representing the systems : Cu(II)-CDTA-en/pn are given in Fig. 1. The other sets involving Ni²⁺ and Zn²⁺ being identical, have been omitted for the sake of brevity.

Curves (a) representing the titration of dihydrochlorides of en and pn exhibits an ill-defined inflection at $m=1$, which may be attributed to the titration of only one of the protons of diamine dihydrochloride.

Well-defined inflections at $m = 1$, depicted in the curves (b) for 1 : 1 Cu(II)-CDTA may probably be correlated to the formation of 1 : 1 Cu(II) — CDTA species. The initial lowering in pH in curves (c) Fig. 1 for 2 : 1 Cu(II) - CDTA system in comparison to that shown by 1 : 1 Cu(II) - CDTA and well-defined inflections at $m = 1$, may be ascribed to the formation of 2 : 1 Cu(II)-CDTA species. Additional inflection at $m = 3$ and appearance of heterogeneous phase may be due to the disproportionation of 2 : 1 species into 1 : 1 species and formation of metal hydroxide.

Curves (d) in Fig. 1 illustrating the titration of the system 2 : 1 : 2 Cu(II) - CDTA-en/pn run parallel and very close to the curves (c) upto $m = 1$. This behaviour may probably be attributed to the initial formation of a soluble 2 : 1 Cu(II) - CDTA species. Another inflection at $m = 5$, preceeded by a long buffer region may be ascribed to the addition of the secondary ligand (en/pn) to the previously formed 2 : 1 Cu(II)-CDTA complex in overlapping steps, resulting in the formation of 2 : 1 : 2 Cu(II) - CDTA-en/pn complex in the system.

The appreciable constancy observed in the values of formation constants (Table 2) of 2 : 1 : 2 complexes provides evidence to the addition of the diamine molecules in two overlapping steps as discussed in our earlier communication[1].

The significant colour changes (from light blue to purple through dark blue), non-superimposable nature of the theoretical composite curves (T) (drawn by adding the horizontal distance of the curves (c) for 2:1 Cu(II) - CDTA, to twice the distances of the curves (a) for en/pn lend additional support to
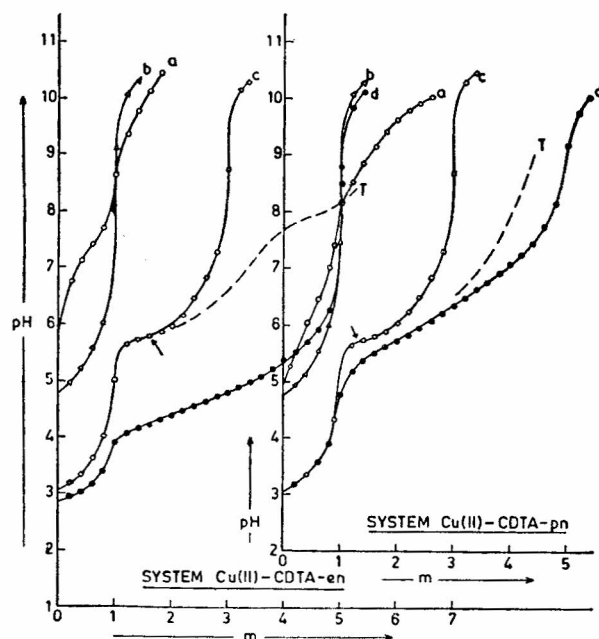

Fig. 1 — Potentiometric titration curves [Curves (a) en/pn; (b) 1:1 Cu(II)-CDTA; (c) 2:1 Cu(II)-CDTA; (d) 2:1:2 Cu(II)-CDTA-en/pn; T, theoretical composite curve; arrow (→) signifies appearance of solid phase]

the formation of a soluble 2 : 1 : 2 Cu(II) - CDTA-en/pn binuclear mixed ligand complexes.

The order of formation constants of the metal complexes in terms of metal ions and diamines is : (i) Zn(II) < Cu(II) > Ni(II) and (ii) pn > en. The order in terms of metal ions is in accordance with the natural order of Irving and Williams[6]. The greater stability of mixed-ligand complexes involving pn (compared to en) is in accordance with the data reported in the literature[7].

The insoluble binuclear mixed-ligand complex Cu(II)-CDTA-HQ (HQ = 8-hydroxyquinoline) has been isolated and tested for its antifungal and antibacterial activities towards some of the fungi (*Penicillium chrysogenum, Aspergillus terrus, Alternaria alternata*) and bacteria (*Staphyllococcus* and Streptococcus). A comparison has been made with the biocidal activities of the free ligands and binary complex, Cu(II)-HQ.

The biocidal activity of the mixed-ligand chelate is considerably higher as compared to the that of the

TABLE 1 — FORMATION CONSTANTS OF BINARY COMPLEXES AT 25° ± 1°

Metal ion	1:1 M(II)-en	1:1 M(II)-pn
Cu(II)	10.65 ± 0.07	10.80 ± 0.08
Ni(II)	7.48 ± 0.08	7.80 ± 0.03
Zn(II)	5.98 ± 0.07	6.00 ± 0.08

TABLE 2 — FORMATION CONSTANTS OF MIXED-LIGAND COMPLEXES AT 25° ± 1° ($\mu = 0.1M$ KNO₃)

System	$\log K^{M_2}_{M_2L}$	$\log K^{M_2E}_{M_2LA}$ Mode-(i)	$\log K^{M_2L}_{M_2LA}$	$\log K^{M_2LA}_{M_2LA+A}$	$\log K^{M_2L}_{M_2LA}$ $+ \log K^{M_2LA}_{M_2LA+A}$	$\log K^{M_2}_{M_2L}$ $+ \log K^{M_2L}_{M_2LA_2}$
			Mode-(ii)			
Cu(II)-CDTA-en	13.28 ± 0.10	13.65 ± 1.48	7.37 ± 0.12	4.49 ± 0.18	11.86	25.14
Ni(II)-CDTA-en	13.12 ± 0.09	10.02 ± 1.42	5.67 ± 0.15	3.80 ± 0.18	9.47	22.58
Zn(II)-CDTA-en	12.69 ± 0.10	13.31 ± 1.32	6.21 ± 0.17	4.98 ± 0.18	11.19	23.88
Cu(II)-CDTA-pn	13.28 ± 0.10	18.93 ± 1.15	9.98 ± 0.14	8.02 ± 0.09	18.00	31.28
Ni(II)-CDTA-pn	13.12 ± 0.09	13.59 ± 1.09	7.36 ± 0.16	5.46 ± 0.10	12.82	25.94
Zn(II)-CDTA-pn	12.69 ± 0.10	11.81 ± 1.00	6.25 ± 0.15	5.33 ± 0.20	11.58	24.27

free metal ion, ligands and binary complex. The higher activity shown by mixed ligand complexes may probably be attributed either to the combined bioactive effects of both the ligands present in the chelate or due to their increased liposoluble nature as a result of coordination to the metal ion. Besides these factors the rapid diffusion of the metal complex through the cell-membrane of fungi and bacteria may be one of the important factors.

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## Potentiometric Determination of Ionization Constants of 3-Phenyl-1-(2'-hydroxyphenyl)-2-propen-1 ones

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The ionization constants of 3-phenyl-1-(2'-hydroxyphenyl)-(PHPO)-, 3-phenyl-1-(2'-hydroxy-5'-methylphenyl)-(PHMPO)-, 3-phenyl-1-(2'-hydroxy-5'-chlorophenyl)-(PHCPO)-, 3-phenyl-1-(2'-hydroxy-5'-bromophenyl)-(PHBPO)-, 3-phenyl-1-(2-hydroxy-5'-nitrophenyl)-(PHNPO)- and 3-(4''-methoxyphenyl)-1-(2'-hydroxyphenyl)-(MPHPO)-2-propen-1-ones have been evaluated potentiometrically at different temperatures, ionic strengths and in solutions of varying dielectric constants. The order of ionization constants is : PHMPO > MPHPO > PHPO > PHBPO > PHCPO > PHNPO. The Hammett's and Born's equations are found to be applicable. The isokinetic temperatures in the range 320-325 K (experimental temperature = 308° K) in all the cases indicate that the process of ionization is enthalpy-controlled.

IN continuation of our earlier work[1-3], we report in this note the ionization constants of 3-phenyl-1-(2'-hydroxyphenyl)-(PHPO)-,3-phenyl-1-(2'-hydroxy-5'-methylphenyl)-(PHMPO)-, 3-phenyl-1-(2'-hydroxy-5'-chlorophenyl)- (PHCPO)-, 3-phenyl-1-(2'-hydroxy-5'-bromophenyl)-(PHBPO)-, 3-phenyl-1-(2'-hydroxy-5'-nitrophenyl)-(PHNPO)- and 3-(4''-methoxyphenyl)-1-(2'-hydroxyphenyl)-(MPHPO)- 2-propen-1-ones, determined potentiometrically at different temperatures and in media of varying dielectric constants and ionic strengths.
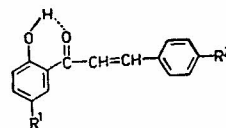
	R¹	R²
PHPO	–H	–H
PHMPO	–CH₃	–H
PHCPO	–Cl	–H
PHBPO	–Br	–H
PHNPO	–NO₂	–H
MPHPO	–H	–OCH₃

The compounds PHPO, PHMPO, PHCPO, PHBPO, PHNPO and MPHPO were perpared by the literature method[4-8], recrystallized from ethanol and their purity checked by TLC and melting point determinations. The solutions of these compounds were prepared in required amounts of absolute ethanol. All other chemicals used were of AR grade. The solutions of nitric acid and KNO_3 were prepared in CO_2—free doubly distilled water.

An ELICO digital pH-meter model LI-120 with glass and calomel electrodes (accuracy $\pm$ 0.01 unit) was used for pH measurements and standardized with buffers of pH 4.00 and 9.20. The pH values in all aquo-organic mixtures were corrected using the method of Van Uitert and Haas[9]. Volume correction was applied by the method suggested by Rao and Mathur[10].

The following solutions were titrated against carbonate-free NaOH solution at three different temperatures :

(i) (a) 10 ml of $1M$ KNO_3 + 70ml EtOH + 10 ml of $0.1M$ HNO_3 + 10 ml H_2O and (b) 10 ml of $1M$ KNO_3 + 60 ml EtOH + 10 ml of $0.1M$ HNO_3 + 10 ml of 0.01 M compound in 100% EtOH + 10 ml H_2O against 0.5 M NaOH and (ii) 10 ml of $1M$ KNO_3 + 60 ml EtOH + 10 ml of $0.01M$ compound in 100% EtOH + 20 ml H_2O against $0.1M$ NaOH. The effects of dielectric constant and ionic strength were studied by determining the pK_a values in solutions of varying concentrations of ethanol and KNO_3 respectively.

The ionization constants were calculated using Bjerrum-Calvin pH titration technique as adopted by Irving and Rossotti[11]. The ionization constants obtained by solving formation function were found to be in good agreement with the values calculated from the Henderson's equation (Table 1). The uncertainity in the pK_a values is of the order of ± 0.02. The pK_a values of the phenols follow the decreasing order : PHMPO > MPHPO > PHPO > PHBPO > PHCPO > PHNPO.

The order of the ionization constants of the acids can be explained based on the strength of the hydrogen