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Potentiometric Determination of the Formation Constants of Complexes of 3,3′,2″-Triaminodipropylethylamine with Co(II), Ni(II), Zn(II) and Cd(II)

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The tripodal tetraamine ligand $N\{(CH_2)_3NH_2\}_2\{(CH_2)_2NH_2\}$ (ppe) has been investigated for the first time as asymmetrical tetraamine chelating agent for cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II). The protonation constants of this ligand and formation constants of its complexes have been determined potentiometrically in 0.1 M KCl at 25°C. The successive protonation constants ($\log K_n$) are: 10.38, 9.68, 8.95 and 3.81 (n = 1-4). One complex has the formula $M(ppe)^{2+}$ is common to the all five metal ions for which the formation constants {$\log \beta_{ML}$, M = Co, Ni, Cu, Zn, Cd} are:, 9.26, 11.95, 15.98, 12.01 and 8.33 respectively. In additon to the simple complex; copper(II), cobalt(II) and zinc(II) also give hydroxo complexes, Copper(II) and nickel(II) give the mono protonated complexes and nickel(II) give the ML_2 complex. The $[Zn(ppe)](ClO_4)_2$ and $[Cd(ppe)Cl](ClO_4)$ complexes were also isolated.

Key Words: Potentiometric, Formation constants, Complexes, Co, Ni, Cu, Zn, Cd, Triaminodipropylethylamine.

INTRODUCTION

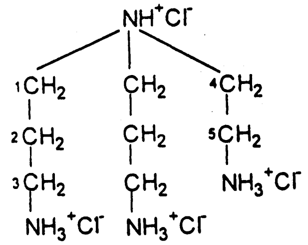
Open chain polyamines have been widely studied owing to their strong ability to bind several metal cations[1–3] and to form fairly stable species, in their protonated form, with organic and inorganic polyanions.[4] The study of polyamine complexes has contributed in large measure to the rationalization of coordination compound formation. Polyamines form stable complexes both in aqueous solution and in the solid state. For example, almost all the metals of the 3d transition series form homogeneous series of polyamine complexes.[5] In general these complexes form rapidly even at room temperature. Because polyamine ligands are fairly strong bases in terms of their affinity for the proton, it has been possible to develop pH-metric techniques which allow the simultaneous determination of both the basicity constants of the polyamine and the complex formation constants.[6] The interaction of the lone pair on the nitrogen atom of an amine with a metal ion spans a considerable range from the very weak 'template assisted' association of alkali and alkaline earth cations[7] to the very robust Co(III) and Ru(III) metal nitrogen bonds. In recent years, tripodal ligands have been of particular interest and many combinations of donor sets have assembled and their protonation constants of their complexes with some metal ions have been determined potentiometrically[8,9]. We have devised improved synthesis of symmetrical and asymmetrical tripodal tetraamines and related ligands.[10–14] The purpose of the present work is to measure the protonation constants of an asymmetrical tripodal ligand, ppe,[13] and formation constants of its complexes with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) at 25°C in 0.1 M KCl. This enabled us to make a comparison with corresponding values under the same condition for some symmetrical and asymmetrical tripodal ligands such as tren,[8] tpt[9] and ppb.[14]

EXPERIMENTAL

Ampoule potassium chloride, use as supporting electrolyte, was obtained as reagent material (BDH). Carbon free solutions of 0.1 KOH were prepared from dilute its ampoules and standardized with potassium phthalate. Metal-chloride stock solutions were standardized by EDTA titration (xylenol orange[15]). IR spectra and NMR spectra were measured on Shimadzu IR-435 and Bruker DPX 300 NMR spectrometers respectively.

Synthesis of Ligand

The ligand tripodal tetraamine (ppe) was prepared as its tetrahydrochloride salt by the literature method.[11] Yield: 5.95g (41%) (found: C, 26.4; H, 8.2; N, 15.2.; $C_8H_{26}N_4Cl_4{\cdot}2{\cdot}5H_2O$; calcd.: C, 26.3; H, 8.49; N, 15.34%). FAB MS (positive FAB in nitrobenzyl alcohol): m/z 175 (ppe H^+, 60%). ^1H NMR δ_H (D_2O, ppm) 2.25 (4H, m, 2-H), 3.2 (4H, t, 1-H), 3.5 (8H, m, 3-H, 4-H and 5-H). ^{13}C NMR D_2O, ppm) 22.8 (C-2), 34.96 (C-4), 37.66 (C-1), 50.47 (C-5), 51.7 (C-3).

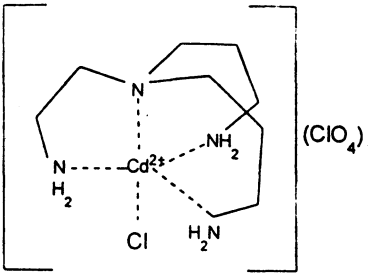


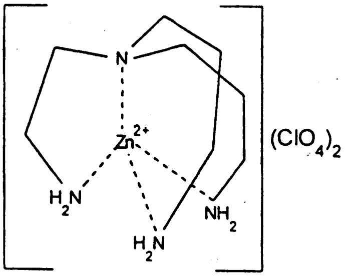
ppe·4HCl

Synthesis of Metal-Complexes: All the metal-complexes were readily prepared by following method. The ppe·4HCl·2.5H_2O (1mmol) and sodium methoxide (about 6 mmol) were refluxed for 20 min. in methanol solution with the metal salt (1 mmol, usually the perchlorate). The solvent was evaporated to small bulk and cooled; crystalline products were usually obtained by slow diffusion of diethyl ether into the solution.

[Zn(ppe)]$(ClO_4)_2$*:* Found: C, 22.42; H, 4.96; N, 12.87%; $C_8H_{22}N_4Cl_2O_8Zn$; requires: C, 21.90; H, 5.05; N, 12.77%. IR (Nujol mull, cm^{-1}): 3313, 3269, 3153 w, 1586 s 1100 vs. ^{13}C NMR δ_c (CD_3CN, ppm): 25.0, 37.0, 43.2, 54.2, 57.1. ^1H-NMR δ_H (CD_3CN, ppm) 1.82 (4H, m), 2.75(6H, m), 3.08 (6H, m), 3.45 (6H, s, N-H).

[Cd(ppe)Cl]ClO$_4$: Found: C, 22.80; H, 5.27; N, 13.03%; $C_8H_{22}N_4Cl_2O_4Cd$; requires: C, 22.73; H, 5.48; N, 13.25%. IR (Nujol mull, cm^{-1}): 3338, 3289, 3168 w, 1588 s 1100 vs.





Potentiometric measurements

Each calibration and potentiometric determination was measured in a 100 cm^3, jacketed cell thermostated at 25°C by refrigerated circulating water bath. Ionic strength was adjusted to 0.100 M by the addition of KCl. Purified (pyrogallol) N_2 was used to degas all solution and to purge the cell during titrations. A 713 Metrohm pH-meter was used with glass and calomel electrodes. A 10 cm^3 capacity Mettler DV11 piston burette was used which delivered standard potassium hydroxide solution directly into the sealed cell through a capillary burette tip which was attached to the cell cap. The apparatus was calibrated on a day-to-day basis by a one-point calibration of dilute strong acid at 0.1 M ionic strength (KCl) in order to measure the hydrogen ion concentration directly.

Procedure

In each system under investigation, the starting volume was 50.0 cm^3, pH measurements were recorded after reagents were added to the sealed system. All titration were carried out by addition of bases to the acid forms of the ligand. pK_w for H_2O at $\mu = 0.1M$ (KCl) at 25°C was found to be 13.78 .

Calculations

The program BEST was used to calculate the equilibrium constants.[16, 17] Species distribution diagrams were computed from the equilibrium constants through the use of programs SPE and the diagrams were plotted on a laser printer with program SPEPLOT.[17]

RESULTS AND DISCUSSION

The tripodal tetraamine ligand (ppe) was prepared by the literature method[11] and was characterized by the ^{1}H-NMR, ^{13}C-NMR, mass spectrometry(FAB) and elemental analyses. Zn(II) and Cd(II) complexes of this ligand were also prepared and were characterized. While the ^{13}C-NMR spectra of both the ligand and its complexes are similar and show, as we expect, five distinct methylene carbons but ^{1}H-NMR spectra are slightly different. This difference is due to coordination of the ligand to metal and the formation of five and six chelate rings in complexes.[18] It seems that, in the case of cadmium complex one chloride ion is coordinated to the 'large' metal ion and its geometry is probably trigonal bipyramidal, but in the case of zinc complex, 'small' metal ion have a tetrahedral structure. The crystal structure of a similar complex, Zn(tpt)$^{2+}$, shows that the zinc ion is encapsulated with the tripodal tetraamine ligand.[19]

Protonation constants: The ligand hydrochlorides were titrated with standard potassium hydroxide, to give the potentiometric equilibrium curves shown in Figure 1. Single inflection point is seen at $a = -3.3$ (a is the number of moles of base added per mole of neutral ligand; negative values indicate base added to the protonated ligand). This corresponds to the neutralization of the one most weakly held protons, which is almost completely dissociated in aqueous solution. The buffer regions ($-3.3 < a < 1.5$) involve the equilibrium for the remaining deprotonation step, for which the equilibrium constants are rather similar. Analysis of the curve yields the successive protonations constants (defined in equations 1 and 2), which are shown in Table-1 along with values for related polyamines.

$$H_{n-1}L^{(n-1)+} + H^{+} \rightleftharpoons H_nL^{n+} \tag{1}$$

$$K_n = [H_nL^{n+}]/\{[H_{n-1}L^{(n-1)+}][H^{+}]\} \tag{2}$$

Comparison with corresponding constants for ppb, tpt and tren shows that the value for each stage is less than the previous stage might have been expected on the bases both of statistical factors and of electrostatic repulsion between the hydrogen ion and the ligand molecule which is successive stage of protonation becomes progressively more positively charged. Thus, four stage of neutralization the constants lie in the order ppb > tpt > ppe > tren. The tertiary nitrogen is largely protonated in ppb and tpt and almost protonated in ppe while in tren it is not, this is obviously due to smaller electrostatic repulsion exerted by three positive poles which are further from the tertiary nitrogen in the above order. Similar trends are seen for all the polyamine ligand. Fig. 2 show the distribution curves for the various protonated forms of ppe, as a function of pH in the absence of metal ions. Over a wide central range, the triprotonated form has the highest concentration.

TABLE-1

PROTONATION CONSTANTS FOR ppe AND RELATED POLYAMINES

	tren[a]	ppe[b]	tpt[c]	ppb[d]
log k_1	10.400	10.378	10.511	10.690
log k_2	9.430	9.682	9.814	10.120
log k_3	8.410	8.952	9.129	9.490
log k_4	—	3.808	5.615	6.720

[a] 2,2′,2″–triaminotriethylamine, Ref. 8.
[b] This work; 25°C $\mu = 0.100$ M (KCl).
[c] 3,3',3″-triaminotripropylamine, Ref. 9.
[d] 3,3′,4″-triaminodipropylbutylamine, Ref. 14.

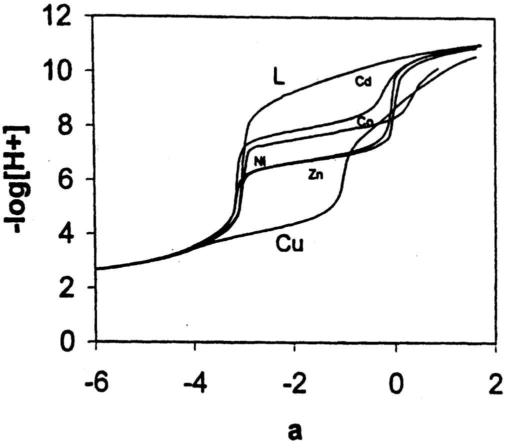


Fig 1. Potentiometric equilibrium curves for ppe(L) and for the 1 : 1 M^{2+} : ppe system; 25°C, $\mu = 0.100$ M (KCl)

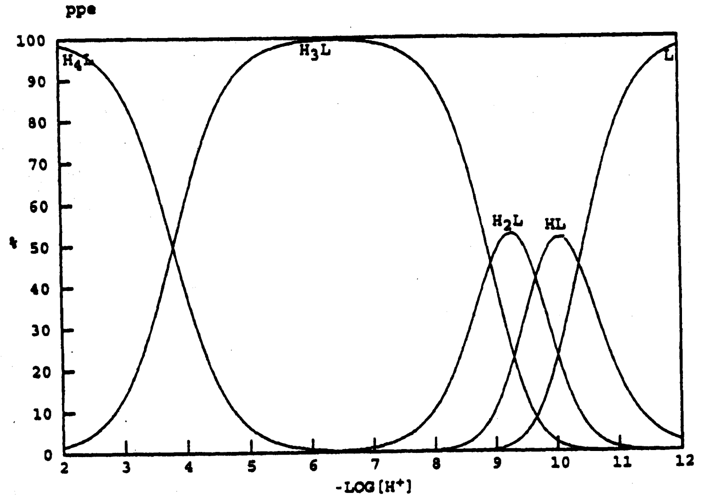


Fig 2. Distribution curves for the protonated ppe (L) species as a function of pH. [ppe] = 1.01 mM, 25°C, $\mu = 0.100$M (KCl).

Formation constants: The potentiometric equilibrium curves for 1 : 1 mol ratios of M^{2+}: ppe (M = Co, Ni, Cu, Zn, Cd) are shown in Figure 1. Complex formation begins at pH 4–8, showing that all four metals are complexed as usual the order of binding is $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, with strong discrimination in the favor of Cu^{2+}. Analysis of the curves shows that, one complex has the formulas ML is common to all four metal ions. In addition to the simple complex; copper(II), cobalt(II) and zinc(II) give hydroxo complexes. Copper and nickel also give mono protonated complexes. Analysis of potentiometric data obtained for two ligands to one metal ion system indicated that only nickel (II) has significant concentration of ML_2 complex, therefore, the experiment was only repeated for nickel(II) at ratios L : M, 2 : 1. Analysis of all the curves allowed formation constants (β, equations 3–6) to be derived for ML and MLH, MLOH and ML_2 complexes. The data are given in Table-2, where they are set against those for complexes of related ligands.

$$M^{2+} + L \rightleftharpoons ML^{2+} \qquad \beta_{ML} = [ML^{2+}]/[M^{2+}][L] \qquad (3)$$

$$M^{2+} + HL^{+} \rightleftharpoons MHL^{3+} \qquad \beta_{MHL} = [MHL^{3+}]/[M^{2+}][H^{+}][L] \qquad (4)$$

$$ML^{2+} + OH^{-} \rightleftharpoons MLOH^{+} \qquad \beta_{MLOH} = [MLOH^{+}]/[M^{2+}][L][OH^{-}] \qquad (5)$$

$$ML^{2+} + L \rightleftharpoons ML_2^{2+} \qquad \beta_{ML_2} = [ML_2^{2+}]/[M^{2+}][L]^2 \qquad (6)$$

Comparisons of log β for the formation of the normal complexes with ppb, tpt, ppe and tren (Table-2) indicate that in spite of lower basicity of tren relative to ppb, tpt and ppe it forms most stable complexes . In fact the order of stability of complexes with the exception of cobalt (II) are $M(tren)^{2+} > M(ppe)^{2+} >$ $M(tpt)^{2+}$ $M(ppb)^{2+}$. The reason for this order must be that ppe complexes have one five- and two six-membered chelate rings, tpt complexes have three six-membered chelate rings and ppb complexes have two six-and one seven-membered chelate rings and it is well known that seven- membered chelate rings are less stable than six-membered rings and both are less stable than analogous five-membered rings. A comparison of the mono, protonated copper(II) complexes with the homologous tetraamines 3,3,2-tetra(ppe), 3,3,3-tetra (tpt) and 3,3,4-tetra (ppb) shows sequence Cu(H-3,3,2-tetra) > Cu(H-3,3,4-tetra) > Cu(H-3,3,3-tetra). In order to understand this behavior we must consider two factors[20]:

(1) The lengthening of aliphatic chain causes a destabilization of the complex. In fact the stability constants of Cu(tpt) (13.511) is lower than Cu(tren) (18.8) (tren = 2, 2′, 2″-triaminotriethyleamine and tpt = 3,3′,3″-triaminotripropylamine).

(2) The removal of the charged NH_3^+ group from the complex causes a higher stability of the complex.

For the case of Cu(H–Cu(H–3,3,4-tetra) and Cu(H-3,3,3–tetra) the stabilizing terms (2) overcomes the destabilizing term (1) and cause order Cu(H—Cu(H-3,3,4-tetra) > Cu(H-3,3,3-tetra). On the other hand the higher stability of Cu(H-3,3,2-tetra) relative to Cu(H—Cu(H-3,3,4-tetra) and Cu(H-3,3,3- tetra) complexes is due to 2,3-system is more stable than 3,3-system

TABLE-2
FORMATION CONSTANTS FOR ppe AND RELATED POLYMINES

M	tren[a]			ppe[b]			tpt[c]			ppb[d]		
	log β_{ML}	log β_{MHL}[e]	log β_{MLOH}[f]	log β_{ML}	log β_{MHL}	log β_{MLOH}	log β_{ML}	log β_{MHL}	log β_{MLOH}	log β_{ML}	log β_{MHL}	log β_{MLOH}
Co	12.80	—	—	9.26	—	8.99	6.36	—	9.35	6.70	14.64	3.14
Ni	14.80	19.17	—	11.95	18.04	—	8.70	15.78	—	6.79	16.09	—
Cu	18.80	—	—	15.98	23.83	22.49	13.12	21.26	17.11	12.98	22.20	15.67
Zn	14.65	—	—	12.01	—	12.59	10.70	—	—	9.37	17.24	9.03
Cd	11.70		—	8.33	—	—	—	—	—	—	—	—

[a] 2,2′,2″-triaminotriethylamine, Ref 8.

[b] This work; 25°C $\mu = 0.100$ M(KCl).

[c] 3,3′,2″-triaminotriethylamine, Ref. 9.

[d] 3,3′,4″-triaminotriethylamine, Ref. 14.

[e] $\log K_1 + \log K_{MHL}$.

[f] $\log K_{ML} + \log K_{MLOH}$.

(note that in all cases the amino group of the longer chain of tetraamine was protonated)[20].

Species-distribution curves: The formation constants allow calculation of the distribution curves for the various complexes as a function of pH, which are shown in Figures 3–8.

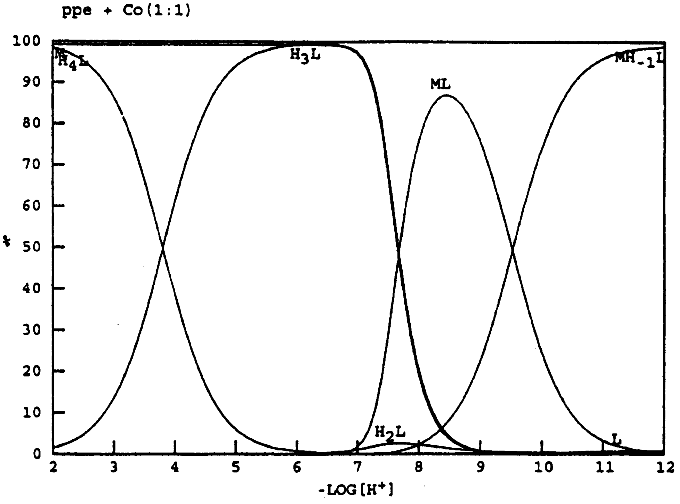


Fig 3. Distribution curves for the Co^{2+}-ppe system as a function of pH, 1 : 1, $[ppe]_{tot}$ = 1.01 mM, $[Co^{2+}]_{tot}$ = 1.0 mM, 25°C, μ = 0.100 M (KCl).

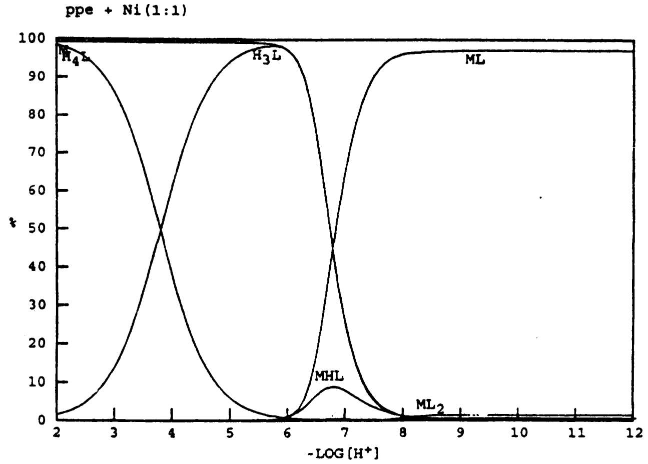


Fig 4. Distribution curves for the Ni^{2+} : ppe system as a function of pH 1 : 1, $[ppe]_{tot}$ = 1.0 mM, $[Ni^{2+}]_{tot}$ = 1.0 mM, 25°C, μ = 0.100 M (KCl).

For copper (II) complexes, in the presence of equivalent amounts of metal and ligand, distribution curves (Fig. 6) shows hydroxo complex $[Cu(ppe)(OH)^+]$, is present as well as mono-protonated and normal copper(II) complexes. Metal complex formation start at about pH 5.5. Distribution curves for nickel(II) complexes (1 : 1 and 1 : 2 metal : ligand ratios, Figs. 4 and 5) show that the complexes formation start at about pH 6.0 and also the normal complex is always exist together either with mono-protonated complex or with biligand complex $Ni(ppe)_2^{2+}$.

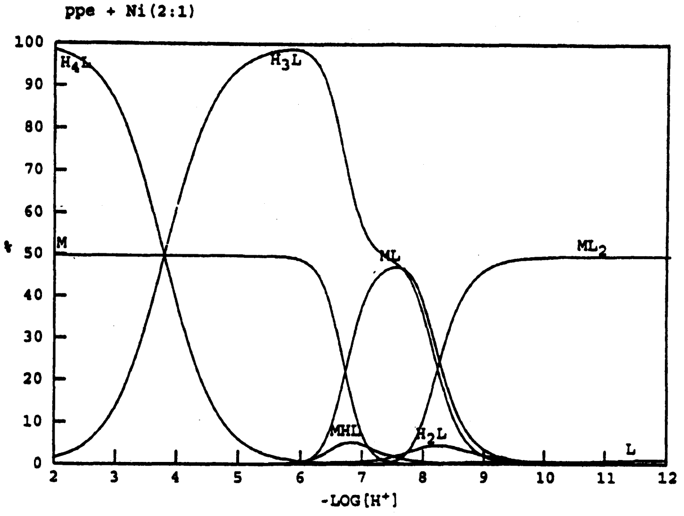


Fig. 5. Distribution curves for the Ni^{2+} : ppe system as a function of pH, 2 : 1, [ppe]= 1.0 mM, $[Ni^{2+}]_{tot}$ = 0.50 mM 25°C, μ = 0.100 M (KCl).

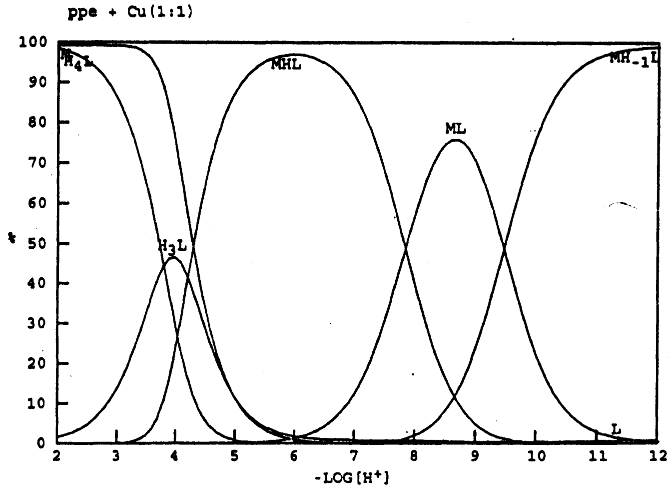


Fig 6. Distribution curves for the Cu^{2+} : ppe system as a function of pH, 1 : 1, $[ppe]_{tot}$ = 1.0 mM, $[Cu^{2+}]_{tot}$ = 1.0 mM .25°C, μ = 0.100 M (KCl)

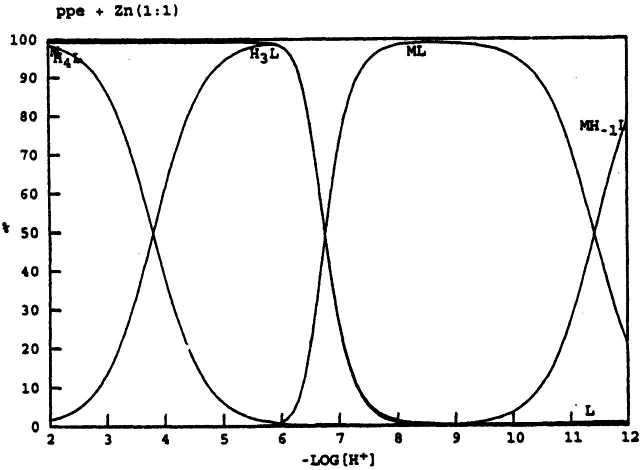


Fig 7. Distribution curves for the Zn^{2+} : ppe system as a function of pH, 1 :1, $[ppe]_{tot}$ = 1.0 mM, $[Zn^{2+}]_{tot}$ = 1.0 mM.25 °C, μ = 0.100 M (KCl).

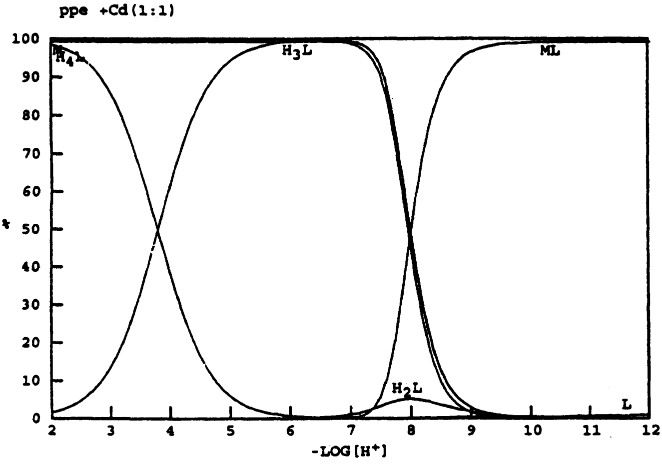


Fig. 8. Distribution curves for the Cd^{2+} : ppe system as a function of pH, 1 : 1, $[ppe]_{tot}$ = 1.0 mM, $[Ni^{2+}]_{tot}$ = 1.0 mM, 25°C, μ = 0.100 M (KCl).

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