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Protonation Equilibrium Studies of H_2BBPEN, H_2BBPPN and H_2BBPBN

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As constantes de protonação dos ligantes hexadentados N,N'-Bis(2-hidroxibenzil)-N,N'-bis(2-metilpiridil) etilenodiamina-H_2BBPEN, N,N'-Bis(2-hidroxibenzil)-N,N'-Bis(2-metilpiridil)-1,3-propanodiamina-H_2BBPPN e N,N'-Bis(2-hidroxibenzil)-N,N'-Bis(2-metilpiridil)-1,4-butanodiamina-H_2BBPBN foram determinadas por espectroscopia UV-visível e titulação potenciométrica com solução padrão de KOH livre de CO_2 a 25.0 ± 0.1 °C, mantendo a força iônica 0.100 M com KCl. A presença de grupos fenólicos, amínicos e piridínicos na molécula fazem com que esses ligantes apresentem uma grande variação no caráter ácido-base dos grupos doadores. Os grupos fenólicos são bastante básicos. Os grupos amínicos desses ligantes apresentam uma basicidade anormal muito baixa e os grupos metilpiridínicos são ácidos fortes.

The protonation constants of the hexadentate ligands N,N'-Bis(2- hydroxybenzyl)-N,N'-Bis(2-pyridylmethyl) ethylenediamine-H_2BBPEN, N,N'-Bis(2-hydroxybenzyl)-N,N'-Bis(2-pyridylmethyl)-1,3-propanediamine-H_2BBPPN, and N,N'-Bis(2-hydroxybenzyl)-N,N'-Bis(2-pyridylmethyl)-1,4-butanediamine-H_2BBPBN, were determined by means of UV-visible spectroscopy and standard potentiometric titration at 25.0 ± 0.1 °C and an ionic strength of 0.100 M KCl. The presence of phenolic, amine and pyridyl donor groups in their molecules means that these ligands show great variation in the acid-base behavior of the donor groups. The phenol groups are very basic, the amine groups show an unusually low basicity, and the pyridylmethyl groups are strong acids.

Keywords: *H_2BBPEN, H_2BBPPN, H_2BBPBN, protonation*

Introduction

Equilibrium studies of ligands which are insoluble or have low solubility in water have been difficult and only partially resolved through the use of water-organic solvent mixtures[1,2,3,4,5]. Some authors utilized pH corrections using empirical equations[6]. Another equation[7] and the Debye-Hückel relationship[8] were used to perform pH corrections for the water-organic solvents used. In most of the articles that appear in the literature, the electrodes are calibrated with standard buffers, and in some corrections are performed for those buffers[5,9,10].

The synthesis of a chelating ligand for a specific metal ion consists of selecting an appropriate donor group to achieve the desired degree of coordination and including them in a ligand framework constructed so as to position them in a favorable location around the metal ion. Thus, the presence of a carboxylate donor group in an amine nitrogen bridge results in a metal complexing yield with poor selectivity for distinguishing between one or another metal ion, due to the high enthalpy and entropy contributions to the metal complex formation. However, higher selectivity may be achieved by replacing one or more carboxylate groups with a corresponding number of coordinating groups having more affinity for the specific metal ion[11,12,13].

Since carboxylate groups are only moderately hard donors, their replacement by negative phenolate groups should improve the selectivity of the ligand for metal ions that are strong acceptors.

The affinity of a ligand modified in this manner for metal ions would tend to be relatively lower, and such a metal ion would therefore not compete as effectively with protons for the very basic phenolate donor group. Similarly, the modification of the ligand structures with the inclusion of constituents containing soft donor groups such as pyridine would greatly lower the affinity of the ligand for a wide variety of electron acceptors such as hard acids. However, the combination of soft and hard donor groups has not been well explored in the complexation of metal ions.

Since it has long been known that the phenolate oxygen donor atoms have very high affinity for the iron(III) ion, building specificity into an aminopolycarboxylic acid ligand by replacing one or more carboxylic group with an appropriate phenol substitute is be expected[13]. Many biological, as well as enzymatic and catalytic phenomena involving transition metals (Fe, Cu, Co, V, Al, Ga, etc.) important for life are still poorly understood, and model systems have been employed in the understanding of the mechanisms governing substrate activation by metal centers[14,15,16,17,18].

According to the three new hexadentate ligands derived from alkyldiamines containing two phenolate-type donors, two α-pyridyl pendant arms, shown in Fig. 1, N,N',N,N'-Bis [(2-hydroxybenzyl)(2-pyridylmethyl)] ethylenediamine-H_2BBPEN, 1, N,N',N,N'Bis[(2- hydroxybenzyl)(2-pyridylmethyl)]-1,3-propanediamine-H_2BBPPN, 2, and N,N',N,N'-Bis [(2-hydroxybenzyl)(2-pyridylmethyl)]-1,4-butanediamine-H_2BBPBN, 3, were synthesized and studied in our laboratory, and the crystal structures of the vanadium(III) and manganese(III) complexes of Ligand 1 were determined[19].

This article aims to present a practical way to perform potentiometric titration in order to determine the protonation constants of these ligands in an aqueous/ethanol mixture, since they have low solubility in water, without using buffers to calibrate the electrodes and approximate methods for pH corrections, and using these equilibrium constants in the calculation of the species distribution of all protonated forms.

Experimental

Abbreviations

H_2BBPEN-N,N',N,N'-Bis[(2-Hydroxybenzyl) (2-pyridylmethyl)]ethylenediamine.

H_2BBPPN-N,N',N,N'-Bis[(2-Hydroxybenzyl) (2-pyridylmethyl)]-1,3-propanediamine.

H_2BBPBN-N,N',N,N'-Bis[(2-Hydroxybenzyl) (2-pyridylmethyl)]-1,4-butanediamine.

EDTA-Ethylene dinitrilo tetraacetic acid.

EBPY-Ethylene bis(iminomethylene-2-pyridine).

TPHEN-Ethylene bis(iminomethylene-2-phenol).

TPEN-Ethylene dinitrilo tetrakis(methylene-2-pyridine).

HBED-N,N'-Bis(2-Hydroxybenzyl) ethylene dinitrilo diacetic acid.

HPED-N,N'-Bis(2-pyridylmethyl) ethylene dinitrilo diacetic acid.

Materials

Pure samples of H_2BBPEN, H_2BBPPN and H_2BBPBN were synthesized using the procedure described in the literature[19b]

Potentiometric measurements

The potentiometric studies were performed in ethanol/water solutions (70/30 %,v/v) due to the low solubility of the ligands in water.The pKw of water in this ethanol/water solution was determined by potentiometric titration of 50 mL of ethanol/water (70/30%, v/v) with a CO_2-free KOH standard. Five experiments were performed. The pKw was found to be 14.71(2), the figure in parentheses representing the standard deviation.

The experimental procedure employed to determine the protonation constants by potentiometric measurements of hydrogen concentration has been described in detail elsewhere[20]. The experimental solutions of each ligand (0.05 mmol) were stocked in a 100 mL thermostated, jacketed reaction vessel with an airtight cap fitted with gas inlet and outlet tubes, glass and reference electrodes and a calomel system. A 10 mL piston burette tip and a magnetic stirrer were used. The Micronal model B 375 pHmeter employed was calibrated with a standard strong acid (HCl) in an ethanol/water solution before starting the titrations.

Each potentiometric titration was done singly. There were usually about 60 points obtained per p[H] profile, providing at least 15 pairs of data (volume, p[H]) per neutralization equivalent. The slope of the response of the electrode was determined using the data obtained from a potentiometric titration of a known volume of a standard 0.010 M HCl in ethanol/water solution (70/30%,v/v) with a standard 0.100 M KOH in ethanol/water solution (70/30%, v/v). The ionic strength of the HCl solution was maintained at 0.100 M by the addition of KCl.

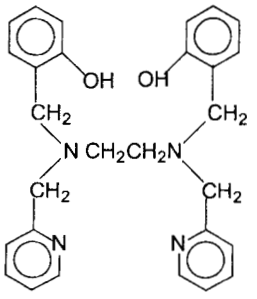
All titrations were carried out at 25.0 ± 0.1 °C and at a 0.100 M ionic strength (KCl) so as to read the hydrogen ion concentration (p[H]) directly, under argon atmosphere with a CO_2-free KOH standard titrant, and the data obtained were analyzed on a PC computer equipped with the Fortran program BEST7[20].

UV-visible measurements

To obtain the equilibrium constants for the phenolic donor group with the proton, all UV-visible measurements were made in ethanol/water solutions (70/30%, v/v), taking

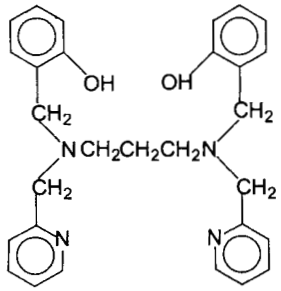
into account the value of 14.71 for the water dissociation constant. UV-visible spectral measurements were made at 25.0 ± 0.1 °C with a Perkin-Elmer model Lambda-19, Fast Scan Spectrophotometer, equipped with 1.000 ± 0.001 cm matched quartz cells. A series of 17 solutions containing appropriate concentrations of KOH and KCl such that [KOH] + [KCl] = 0.100 M, to cover the range of 10.71 to 13.0 pH units, with a 1.0 x 10^{-4} M concentration of each ligand in solution, were measured between 200 and 350 nm, under the conditions described above. At higher KOH concentrations (p[H] above 13.0) the ionic strength was not controlled.

Figure 2 shows the spectral variations of the H_2BBPEN ligand with p[H]. The other two ligands have shown analo-



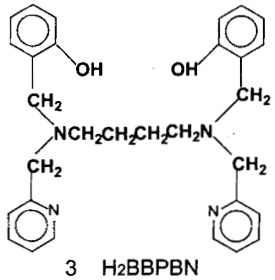
1 H_2BBPEN

N,N',N,N" BIS[(2 - HYDROXYBENZYL) (2 -PYRIDYLMETHYL)]ETHYLENEDIAMINE



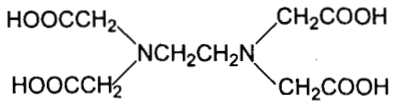
2 H_2BBPPN

N,N',N,N" BIS[(2 - HYDROXYBENZYL) ($_2$ - PYRIDYLMETHYL)] PROPANEDIAMINE



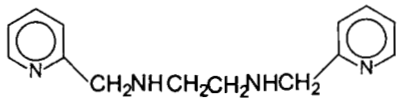
3 H_2BBPBN

N,N',N,N" BIS[(2 - HYDROXYBENZYL) (2 -PYRIDYLMETHYL)] BUTHYLENEDIAMINE



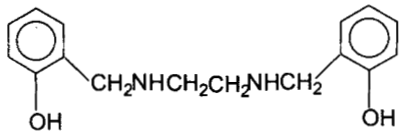
4 EDTA

ETHYLENE DINITRILO TETRAACETIC ACID



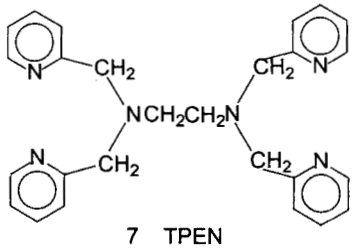
5 EBPY

ETHYLENE BIS(AMINOMETHYLENE - 2 - PYRIDINE)



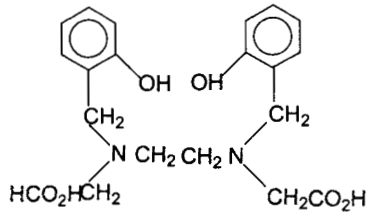
6 TPHEN

ETHYLENE BIS(IMINOMETHYLENE - 2 - PHENOL)



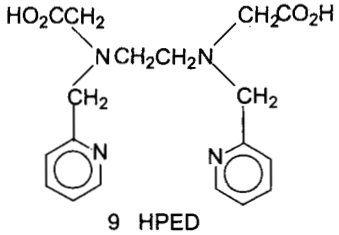
7 TPEN

ETHYLENE DINITRILO TETRAKIS (METHYLENE - 2 - PYRIDINE)



8 HBED

N,N'-BIS (2 - HYDROXYBENZYL) ETHYLENE DINITRILO DIACETIC ACID



9 HPED

N,N'-BIS(2-PYRIDYLMETHYL) ETHYLENE DINITRILO DIACETIC ACID

Figure 1. Ligand structures: 1, H_2BBPEN; 2, H_2BBPPN; 3, H_2BBPBN; 4, EDTA; 5, EBPY; 6, THPEN; 7, TPEN; 8, HBED; 9, HPED.

gous behavior. The absorbance at each p[H] at a given wavelength was calculated as described[21] from data taken in the UV-visible spectra of the ligand. The chosen wavelength was 296 nm, which corresponds to the characteristic phenolate maximum absorbance. The equilibrium constants were calculated using the Fortran program ABSPKAS[22].

Results and Discussion

The protonation constants of H_2BBPEN, H_2BBPPN and H_2BBPBN defined by Eq. 1 are presented in Table 1, along with similar constants for other chelating agents[23,24,25,26,27,28,29].

$$L + nH^+ \rightleftharpoons H_nL; \quad K_n = [H_nL]/[H_{n-1}L][H^+] \quad (1)$$

For each ligand, the first two protonation constants were attributed to the phenolate groups and were determined by UV-visible measurements, since their values were too high to be determined by potentiometric titration.

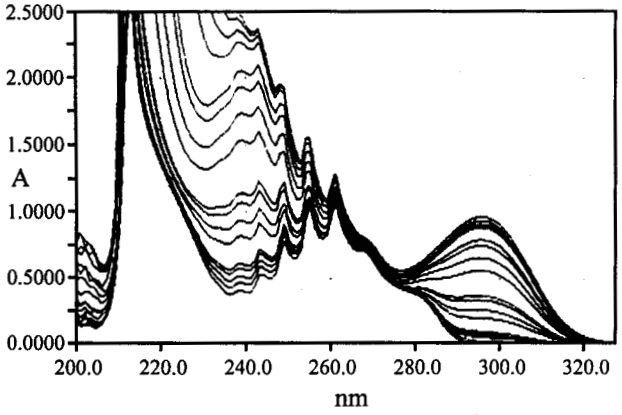


Figure 2. UV-visible spectra of H_2BBPEN in a 1.0 x 10^{-4} M ethanol/water, (70/30%, v/v), solution, in the p[H] range 10.71 (lower line), 11.20, 11.42, 11.62, 11.72, 12.20, 12.42, 12.65, 12.75, 13.20, 13.42, 13.63, 13.72, 14.19, 14.42, 14.61 and 14.71 (upper line); at T = 25 ± 0.1 °C, and μ = 0.100 M (KCl).

The ultraviolet absorption spectra of the H_2BBPEN ligand as a function of p[H] are shown in Fig. 2. The equilibria involve two phenol-phenolate systems. The totally deprotonated species has an absorption maximum at 296 and 240 nm, and the deprotonated species has zero absorbance at 296 nm and 0.4815 at 240 nm. The measured absorbance is the sum of the products of the molar extinction coefficient ε_{HnL} (n = 0, 1, 2) and the concentration of the corresponding species, H_nL (Eq. 2). A and ε_{HnL} must correspond to the same wavelength.[23] The total ligand concentration is also known (Eq. 3).

$$A = \sum_{0}^{2} \varepsilon_{HnL} [HnL] \quad (2)$$

$$L^t = \sum_{0}^{2} [HnL] = \sum_{1}^{2} K_n{}^H [H^+][H_{n-1}L] \quad (3)$$

The first and second protonation constants were calculated by solving Eqs. 2 and 3 for each experimental point using the computer program ABSPKAS[22]. The program adjusts ε_{HnL} and K_nH by comparing the calculated A values with the experimental ones. The calculated constants are shown in Table 1.

The titration curves for the ligands are shown in Fig. 3. The first break appears at a = 3 for H_2BBPEN and means that the addition of 3 mmol of KOH per mmol of ligand neutralizes three mmols of protons at pH values lower than 4.0. The second break occurs roughly at a = 4, indicating that the four protons of the ligand are neutralized at this point. The experiment was interrupted by the precipitation of the ligand at pH values above 6.5. The buffer region around 6 means that a protonation step occurs due to the

Table 1. Logarithms of protonation constants of H_2BBPEN, H_2BBPPN, H_2BBPBN and related ligands[a].

	log (quotient)								
quotient	EDTA[b]	EBPY[b]	TPHEN[b,e]	TPEN[b,d]	HBED[b]	HPED[b,e]	H_2BBPEN[c]	H_2BBPPN[c]	H_2BBPBN[c]
HL/H.L	**10.19(4)**	8.22(6)	10.50	**7.19**	12.53(7)	**8.84**	13.26(5)	13.27(5)	13.17(5)
H_2L/HL.H	**6.13(3)**	5.40(7)	9.80	**4.85**	11.00(1)	**5.63**	12.00(5)	11.97(5)	11.97(5)
H_3L/H_2L.H	2.69(5)	1.8(3)	**8.37**	3.32	**8.38(6)**	3.02	**5.99(2)**	6.09(2)	**6.14(2)**
H_4L/H_3L.H	2.0(1)	1.6(2)	**6.17**	2.85	**4.68(4)**	2.34	**3.11(2)**	4.12(3)	**4.86(3)**
H_5L/.H_4L.H	1.5(1)								
H_6L/H_5L.H	0.0(1)								

a. 25.0 ± 0.1 °C and μ = 1.0 , the standard deviations are reported in parentheses and represent the deviation in the last figure.
b. Ref. 29.
c. In this work, σ_{fit}= 0.002388: σ_{fit} is the standard deviation computed from calculated p[H] values relative to those experimentally observed[20]. The log K values in bold figures are due to the protonation of the amine groups in the ligands.
d. 20 °C and μ = 0.1, standard deviation not reported.
e. Standard deviation not reported.

third protonation of the ligand. The first two protonations occur at higher pH values at the phenolate groups as described in the UV-visible section, while the fourth protonation occurs at pH values lower than 4.0. Curves 2 and 3 can be described in the same way, and the protonation constants are shown in Table 1.

Although H_2BBPEN, H_2BBPPN and H_2BBPBN each differ by a $-CH_2-$ unit, there are small differences in the p[H] profile for these compounds. These differences are due to the protonation constants of each one. The protonation constants assigned on the basis of the order of basicity, phenolate > amine > pyridyl, are due to the two phenolate groups, two amine groups and two pyridyl groups which are very low (strong acids) and were not determined. Scheme 1 shows the protonation steps for H_2BBPEN. The major difference is in the fourth protonation constant, which increases about one log unit as a $-CH_2-$ unit is added to the structure of the ligand. This behavior can be understood on the basis of increasing a $-CH_2-$ unit, which makes one side of the ligand more independent with respect to the protonation of the groups on the other side.

Protonation of one amine group of H_2BBPBN (log K_3 = 6.14) has less effect on the second amine group (log K_4 = 4.86) when compared with the protonation of the same groups in H_2BBPEN, log K_3 = 5.99 and log K_4 = 3.11. In other words, it is more difficult to protonate the second amine group in H_2BBPEN. The proximity of the protonated amine group to the second one which is not protonated as in 12 (Scheme 1) makes a stabilizing effect of the hydrogen bond possible. Thus, protonation of the second amine nitrogen group is more difficult, requiring a higher concentration of protons. However, the formation of a hydrogen bond involving the two amine groups in H_2BBPBN is less effective because they are separated by four $-CH_2-$ units.

The three ligands (H_2BBPEN, H_2BBPPN and H_2BBPBN) have two pyridylmethyl and two methylphenol groups attached to the amine the bridge. The first two protonation constants are somewhat higher than those for HBED (Table 1), which also has two phenolate groups in its structure (Fig. 1), and these differences are attributed to the solvent. The constants for HBED were calculated in an aqueous solution, while these studies were done in ethanol/water solutions (70/30 %, v/v).

The protonation of the amine group of the EDTA (Fig. 1) corresponds to the first protonation (Table 1). It is about two log units higher than the same protonation in the EBPY, TPHEN, TPEN, HBED and HPED ligands, and about three log units higher than H_2BBPEN, H_2BBPPN and H_2BBPBN. This effect is attributed to the four negative carboxylate groups surrounding the amine nitrogens in the EDTA ligand, which increase the first protonation in the amine groups. Comparing the ligands of Table 1, H_2BBPEN presents the lowest protonation constant of the first amine group. The presence of two phenolate groups as

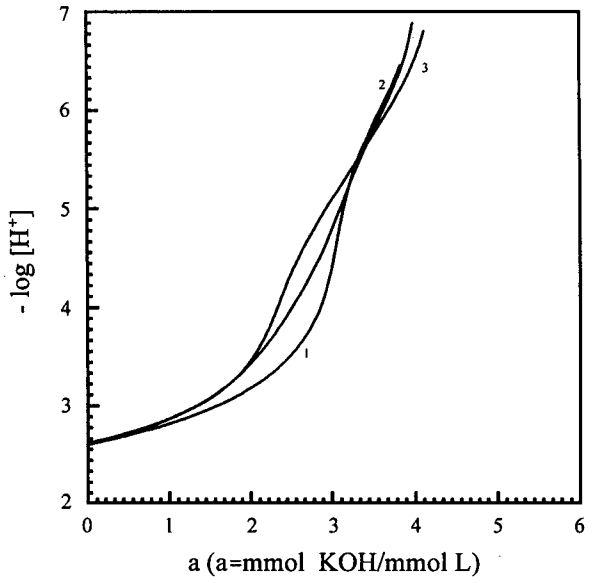
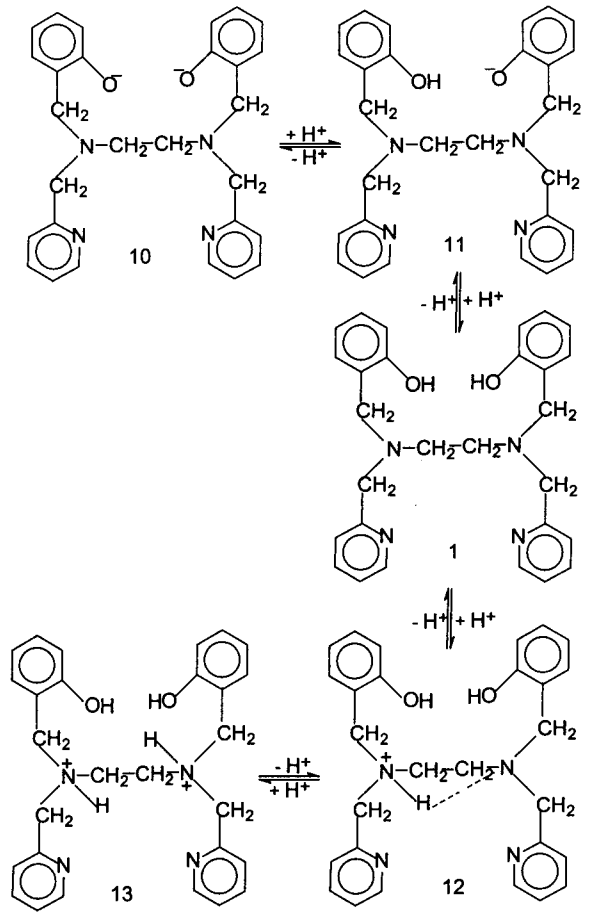


Figure 3. Potentiometric p[H] profiles for 1.0×10^{-3} M solutions of 1, H_2BBPEN; 2, H_2BBPPN; 3, H_2BBPBN; at T = 25 ± 0.1 °C; and μ = 0.100M (KCL).



Scheme 1.

in TPHEN, or two 2-methylpyridyl groups as in EBPY, seems to interfere in the same way in the first protonation of the amine groups (TPHEN, log K_3 = 8.37; EBPY, log K_1 = 8.22). However, additional groups attached to the amine entity, as in the TPEN, HBED, HPED and H_2BBPEN ligands, have different effects on the protonation of the first amine group. The addition of two pyridylmethyl groups in the EBPY structure yields the structure of the TPEN ligand. These two additional pyridylmethyl groups lower the first protonation constants of the amine groups by almost one log unit. On the other hand, the addition of two methylcarboxyl groups to the structure of the TPHEN ligand, yielding HBED, has no effect on similar protonation constants, although the basicity of the phenol groups increased, their protonation constants being almost two log units higher. However, the addition of two methylcarboxyl groups to the EBPY ligand structure, yielding HPED, somewhat increases the protonation under consideration.

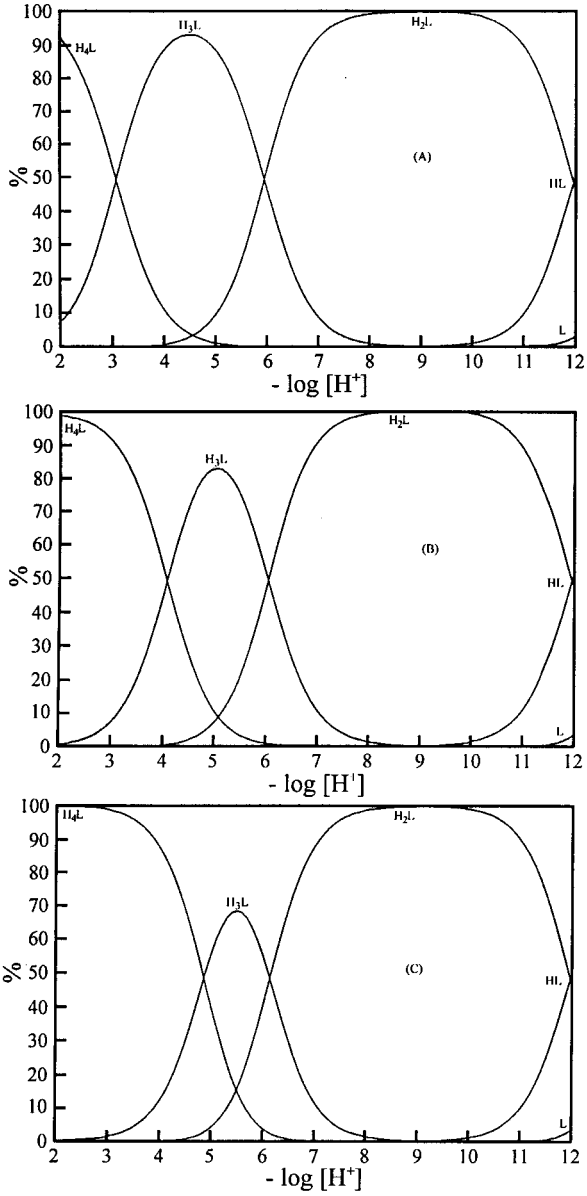


Figure 4. Species distribution curves for 5.0 x 10^{-4} M solutions of the ligands: A, H_2BBPEN; B, H_2BBPPN; C, H_2BBPBN; where L is the complete deprotonated species and HL, H_2L, H_3L, H_4L are the mono-, di-, tri and tetra protonated species of the ligands; at T = 25 ± 0.1 °C and μ = 0.100 M (KCL). %, is the percent of the species present set at 100%.

The biggest effect on the first protonation of the amine groups is observed with the H_2BBPEN ligand. The addition of two pyridylmethyl groups to the structure of TPHEN lowered the protonation by more than two log units (Table 1). The second protonation of the amine groups was also lowered. Its protonation constant is about three log units lower, and the basicity of the phenol groups increased.

The protonation of pyridylmethyl groups in H_2BBPEN, H_2BBPPN and H_2BBPBN is very low; they are strong acids, as in the TPEN ligand. In the TPEN ligand two pyridylmethyl groups have higher protonation constants than those in EBPY, and two are strong acids. The protonation constants determined for the H_2BBPEN, H_2BBPPN and H_2BBPBN ligands were used to draw the species distribution curves in Fig. 4. Indeed, the curves are very similar to each other. The major difference is related to the maximum of the triprotonated species of each ligand. The protonated species for the H_2BBPEN ligand are shown in A (Fig. 4). The higher concentration of the triprotonated form occurs at p[H] = 4.5, where it is 93% formed. On the other hand, the triprotonated species of H_2BBPPN is 84% formed at pH = 5.1 (Fig. 4, B), and the same species for the H_2BBPBN ligand is at its maximum at p[H] = 5.6, where it is 69% formed (Fig. 4 C).

The conditions for potentiometric and spectrometric studies for H_2BBPEN, H_2BBPPN and H_2BBPBN ligands and their protonation constants in ethanol/water solutions has been determined. The results will be used for equilibrium studies of the complex formation of these ligands with divalent and trivalent metal ions. These studies are in progress and the results will be published in the near future.

Acknowledgments

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