Potentiometric study of equilibrium constants of a novel triazine–thione derivative and its stability constants with Hg^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} metal ions in ethanol and water mixed

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Abstract: The deprotonation constants of 5-hydroxy-5,6-di-pyridin-2-yl-4,5-dihydro-2H-[1,2,4] triazine-3-thione (HPT) and the stability constants of its Hg^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ion complexes were studied in 20% ethanol and water mixed at 25 ± 0.1 °C and ionic strength (I) of 0.1 M supported by NaCl. Four pK_a values of HPT were determined: 3.58, 6.30, 9.23, and 9.69. In various pH conditions, the different complex forms were formulated as ML, MHL, MH_2L, MH_3L, MH_4L, and $MH_{-2}L$ between Hg^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions and HPT. According to the potentiometric and spectrophotometric results, the HPT and Hg^{2+} combination formed a selective and highly stable complex at pH 7.

Key words: Potentiometry, triazine–thione, equilibrium constants, proton affinity

1. Introduction

Schiff base macroligands were derived from thiosemicarbazide and their complexes are of significant interest for their pharmacological properties as antibacterial and anticancer agents.[1−3] In addition, triazine derivatives have traditionally found application in analytical chemistry as complexation agents, in electrochemistry as multistep redox systems, and as pesticide or herbicide components in agriculture.[4] Moreover, triazine derivatives have been successfully used in the development of potetiometric sensors for determination of some toxic metals.[5] The binding and speciation in systems containing Cu^{2+} and Zn^{2+} ions and suitable ligands are of interest in diverse fields, including medical diagnostics, toxicological studies, and environmental pollution.[6] The accidental liberation of mercury in the environment causes dreadful toxicity problems, but recent studies have considered the reactivity of macroligands containing sulfur to entrap this metal.[7,8]

Stability constants of metal complexes were determined by many different methods, such as spectrophotometry and potentiometry. It is well known that the simplest electro-analytical technique for determination of stability constants is a potentiometric titration system used for glass electrodes. The 1,2,4-triazine-thiones are well-known compounds, and a variety of synthetic methods for the preparation of substituted derivatives are available. Acid dissociation constants are particularly important in pharmaceutical research, especially for the discovery and evaluation of new compounds that could be pharmacologically active, i.e. potential drugs.[9]

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In the present research, the dissociation constants of a newly synthesized ligand, 5-hydroxy-5,6-di-pyridin-2-yl-4,5-dihydro-2H-[1,2,4]triazine-3-thione (HPT), and the stability constants of its divalent metal complexes were determined at 25 °C in NaCl (I = 0.1 M) potentiometrically.

2. Experimental

2.1. Reagents

HPT was previously synthesized and characterized by Cukurovali.[10] The chemical structure of HPT is given in Figure 1.
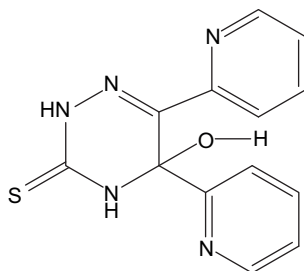
Figure 1. Chemical structure of HPT.

All reagents were of analytical quality and were used without further purification. Sodium hydroxide (Merck) and potassium hydrogen phthalate (Fluka) were dried at 110 °C before they were used. For calibration of the electrode systems 0.05 m potassium hydrogen phthalate (KHP) (Fluka) and 0.01 m borax ($Na_2B_4O_7$) (Fluka) were prepared. Moreover, 1.10^{-3} M HPT in 20% ethanol–water mixed, 1.10^{-3} M metal solution, 0.025 M NaOH, and 0.1 M HCl (J.T. Baker) were prepared. HPT is not soluble enough in water. Therefore, it was dissolved in 20% ethanol–water mixed for providing homogeneous solution media and 1×10^{-3} M HPT stock solution was prepared. $CuCl_2$, $ZnCl_2$, $PbCl_2$, $HgCl_2$, and $NiCl_2$ were purchased from Merck. Also 1.0 M NaCl (Riedel-de Haën) stock solution was prepared. For the solutions, CO_2-free deionized water was obtained using an aquaMAX^{TM}-$Ultra$ water purification system (Young Lin Inst.). Its resistivity was 18.2 MΩ cm^{-1}.

pH-metric titrations were performed by using a Molspin pH meter^{TM} with an Orion 8102BNUWP ROSS Ultra combination pH electrode. The temperature in the double-wall glass titration vessel was constantly controlled using a thermostat (DIGITERM 100, SELECTA) and kept at 25.0 ± 0.1 °C. The cell solution was stirred during the titration at constant speed. The electrode was calibrated according to the instructions of the Molspin Manual.[11] An automatic burette was connected to a Molspin pH-mV-meter. In this study, 20% ethanol–water mixed was used for preparing 1×10^{-3} M HPT stock solution and the stock solution was diluted at 1:10 ratio in all experiments. There was only a trace amount of organic solvent in the titration cell. Therefore, the pH electrode was calibrated with potassium hydrogen phthalate and borate buffer solution at 25.0 (±0.1) °C.[12] During the titration, nitrogen (99.9%) was purged through the cell. The SUPERQUAD computer program was used for the calculation of both protonation and stability constants.[13]

2.2. Procedure

First, the ligands were dissolved in ethyl alcohol and then the solutions were diluted with deionized water. The final concentration of the ligands was 1.10^{-3} M and their final water:ethyl alcohol ratio (v/v) was 80:20. Stock 0.025 M sodium hydroxide and 0.1 M HCl solution were prepared. Solutions of 1.10^{-3} M metals ions were

prepared from $CuCl_2$, $ZnCl_2$, $PbCl_2$, $HgCl_2$, and $NiCl_2$ and standardized with ethylenediaminetetraacetic acid (EDTA).[14] The ionic strength was adjusted to 0.1 M with sodium chloride. The potentiometric titrations were performed using a Molspin pH meter?[U+F8EA] with a Sentix 20 pH combined electrode (WTW, Weilheim, Germany). The temperature was controlled by a thermostat (DIGITERM 100, SELECTA) at 25.0 ± 0.1 °C. The titration vessel was double-wall glass and it was placed on the magnetic stirrer. It was cleaned with distilled water and dried with a tissue before and after each titration. The vessel was covered by the lid, which contained 3 holes for the electrode, glass tubing for nitrogen purging, and plastic tubing for alkali from the burette. The electrode was calibrated according to the instructions in the Molspin manual. No air bubbles were allowed to leak in the syringe while filling with an alkali solution. Before filling with a solution, the syringe was washed several times with distilled water and rinsed at least 3 times with the alkali. Titration was performed in triplicate, and the SUPERQUAD computer program was used for the calculation of protonation and stability constants. A summary of the experimental parameters for the potentiometric measurements is given in Table 1. The standard deviations quoted refer to random errors only. The pH data (250) were obtained after addition of 0.03 cm^3 increments in the standardized NaOH solution. The pK_w value of the aqueous system on the ionic strength employed, defined as $-\log [H^+][OH^-]$, was obtained as 13.98.

Table 1. Summary of the experimental parameters for the potentiometric stability constant measurements.

| System: HPT with H^+, Cu^{2+}, Ni^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} in water |
|---|
| Solution composition: [L] range / M 0.001–0.002 [M] range / M 0.001 ionic strength / M 0.1 electrolyte NaCl |
| Experimental method: Potentiometric titration in range pH 3–11 log β_{00-1} – 13.98 |
| T/°C: 25.0 |
| n^a_{tot}: 250 |
| n^b_{tit}: 3 |
| Method of calculation: SUPERQUAD |
| Titration system: MOLSPIN |

^{a} Number of titration points per titration, ^{b} Number of titrations per metal ligand system, M: Metal ion, L: ligand, β: overall stability constant

3. Results and discussion

3.1. Dissociation constants

The chemical structure of HPT is given in Figure 1. Potentiometric titration of this compound with NaOH was performed in 0.1 M NaCl at 25 °C. The titration curve of the ligand is given in Figure 2.

Four pK_a values for HPT were calculated by SUPERQUAD using titration data (see Table 2). The pK_a values were 3.58, 6.30, 9.23, and 9.69. While pK_{a1} and pK_{a2} values are related to the pyridine groups, pK_{a3} and pK_{a4} values are related to S and N atoms in the triazine–thione group. According to Cukurovali,[10] the hydroxyl group forms a hydrogen bond with the nitrogen atom of a pyridine ring, and we assume that the nitrogen atom gains a δ^+ charge. Consequently, the acidity of the nitrogen atom increases and its pK_a value decreases. The negative charge density of the nitrogen atom in the other pyridine ring rises because of increasing conjugation and its pK_a value. According to our experimental results, thione form was easily transformed into thiol form depending on pH (see Figure 4). This case was reported in many studies in the literature.[10,15,16] Therefore, the protonation constants of the S atom in the triazine–thione group could be determined in this study.
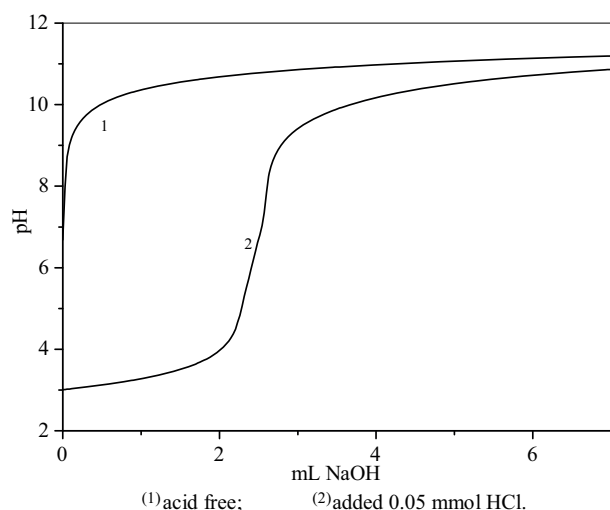
Figure 2. Potentiometric titration curve of HPT (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, $I = 0.1$ M by NaCl).
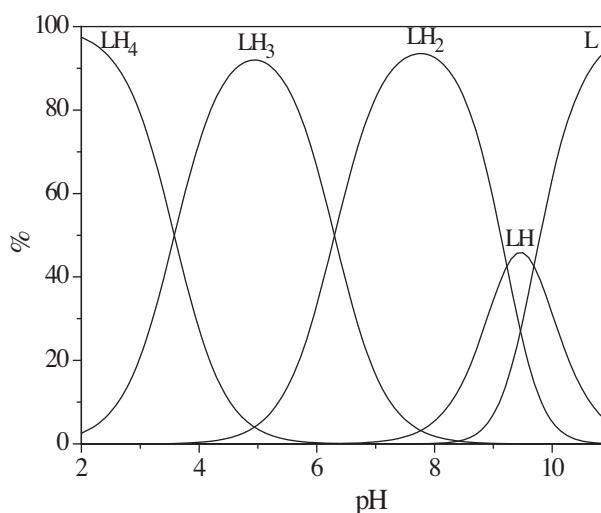
Figure 3. Distribution curves of HPT (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, $I = 0.1$ M by NaCl, 0.05 mmol HCl).
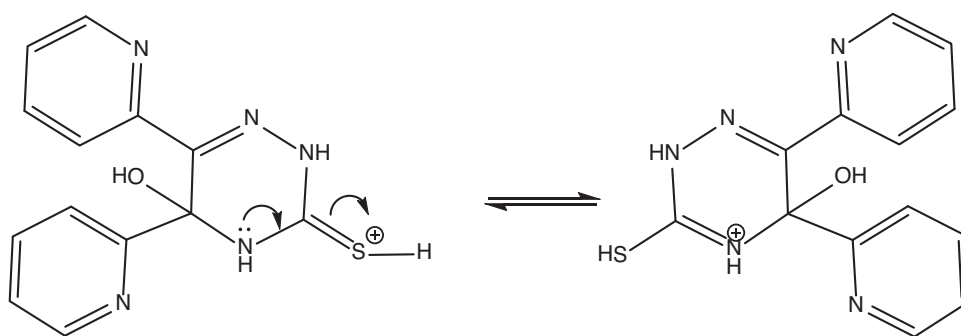
Figure 4. Mechanism of the thione–thiol tautomerism in HPT.

There might be differences in protonation orders of atoms in HPT due to the forming of a hydrogen bond between the hydroxyl group and nitrogen atom of a pyridine ring and forming of an acid thiol group because of tautomerism in the ligand.

Four protonated species formulated as LH_4, LH_3, LH_2, and LH were observed during titration processes. The deprotonation equilibrium is as seen in the following equations (charges are omitted for simplicity):

$$LH_n \rightleftharpoons LH_{n-1} + H \tag{1}$$

and the deprotonation constants (K_n) are given as

$$K_n = [LH_{n-1}][H]/[LH_n].$$

All species have a broad protonation space between pH 3 and 11. When pH increases, the protonated ligand losses protons and it is converted to the other forms as seen in Figure 3. It is assumed that high acidity causes the protonation of the nitrogen atom on HPT and decreases the mobility of its π-electrons. The concentration levels of LH_4, LH_3, LH_2, and L are above 90%, while that of LH is 40%. The free ligand (L) starts to form at pH 8 and reaches its maximum at pH 11 (90%–95%).

Table 2. Dissociation constants (pK_a) of HPT (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, $I = 0.1$ M by NaCl, 0.05 mmol HCl).

Ligand	Species	$\log_{10}\beta$	pK_a values
HPT	LH_4	28.80 ± 0.05	3.58
	LH_3	25.22 ± 0.03	6.30
	LH_2	18.92 ± 0.03	923
	LH	9.69 ± 0.03	9.69

As a result of dissociation of donor atoms of the ligand, free electron pairs are placed in empty valance orbitals of metal ions. Therefore, metal–ligand coordination occurs. In other words, complexation starts with the proton transfer reaction. In this regard, the obtained dissociation constants play an important role in explaining metal–ligand coordination.

3.2. Stability constants

According to the electronic delocalization, which is enhanced upon deprotonation, HPT is very versatile. This fact, together with the presence of different types of donor atoms, makes several coordination modes possible.[17,18] Therefore, depending on the metal coordination preferences, the ligand can show different coordination behavior.[19] The potential coordinating sites are sulfur atoms of the thiol group, and nitrogen atoms of the pyridine and triazole groups. Thus, HPT can also be polydentate. It has been shown and experimentally verified that bidentate or multidentate ligands, in general, form more stable complexes than monodentate ligands do.[20] Since metal ions of class 'a' have a preference for nitrogen (hard) donors, and class 'b' have preference for soft (sulfur) donors, it would be interesting to investigate this aspect by using both types of metal ions, as HPT contains both hard nitrogen and soft sulfur donor atoms.[21] There has been considerable interest in HPT containing more different donor atoms because such ligands shed light on the nature of metal–ligand bonding. Many quantitative studies have confirmed that such metal chelates are more stable than unidentate ligands. Furthermore, 5- or 6-membered stable chelates are by far the most common ones and are, in general, the most stable.[22,23]

The complex solutions were titrated with standard 0.025 M NaOH solution to determine the stability constants of complexes formed by divalent metal ions (M) and the ligand (L). The data obtained from M^{2+}–HPT titrations were evaluated by using the SUPERQUAD program and the overall stability constant data for the complexation of Hg^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} with HPT are given in Table 3.

Table 3. Stability constant data for the complexation of Hg, Ni, Cu, Pb, and Zn with HPT at 25 °C, $I = 0.100$ M NaCl in aqueous solution.

| Complex	mhl	Hg	Ni	Cu	Pb	Zn
M-HPT	101	12.32 ± 0.03	4.92 ± 0.08	8.13 ± 0.07	5.80 ± 0.09	6.84 ± 0.03
	111	20.86 ± 0.04	-	16.80 ± 0.04	14.77 ± 0.04	16.50 ± 0.06
	121	26.34 ± 0.03	24.43 ± 0.06	23.40 ± 0.03	-	24.11 ± 0.12
	131	-	33.35 ± 0.07	-	-	32.68 ± 0.07
	141	-	37.67 ± 0.06	-	-	35.81 ± 0.08
	1-21	-6.404 ± 0.02	-14.82 ± 0.07	-11.36 ± 0.09	-14.13 ± 0.12	-13.63 ± 0.11

*m: number of metals, h: number of hydrogens (positive values) or hydroxides (negative values), l: number of ligands in the complex.

Various complexes formulated as ML, MHL, MH$_2$L, MH$_3$L, MH$_4$L, and MH$_{-2}$L between the ligand and metal ions are formed depending on pH. As seen in Table 2, their magnitude is in the order Hg > Cu > Zn > Pb > Ni for the complex ML type. The stability constant of Hg (12.32 ± 0.03) is the highest. The titration curves are given in Figure 5.

There are 2 inflection points in the titration curve apart from Ni^{+2}. Although the experimental conditions are similar, their inflection points are different from each other because of the various degrees of hydrolysis of metal ions. When the hydrolysis degree of M^{2+} is increased, the inflection point of the complex system shifts to the right.[24] The interactions of M^{2+} with L (1:1) lead to the formation of ML-type complexes. Comparing the titration curves, the complex curves are situated just further than the free ligand curve as they required more alkali to have the same pH as the free ligand. This case can be explained as a result of proton release from the coordinated ligand, which implies complex formation. The amount of protons released depends on the strength of the metal–ligand bond.[25]
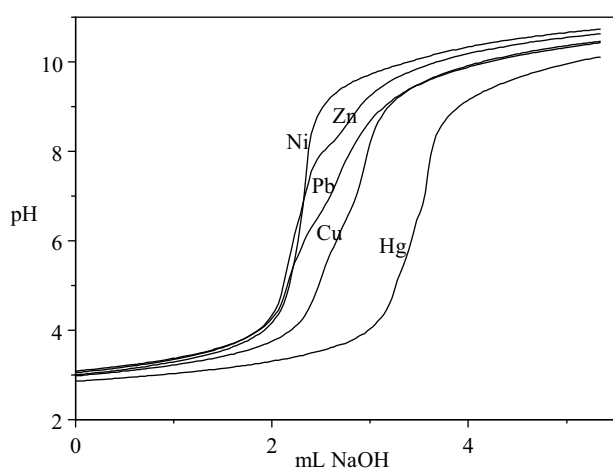

Figure 5. Titration curves for M^{2+}–HPT (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, I = 0.1 M by NaCl, 0.05 mmol HCl).
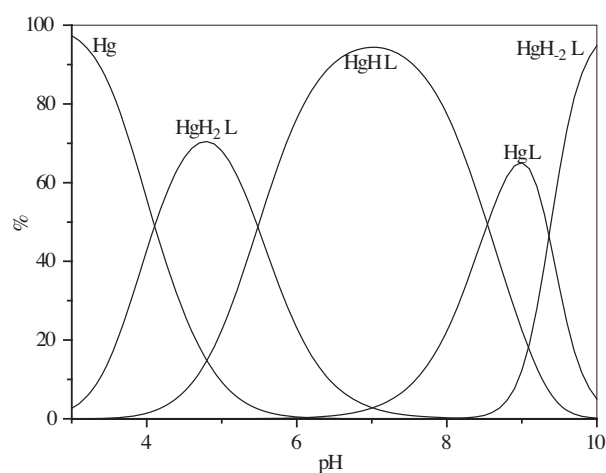
Figure 6. Species distribution curves for the Hg–HPT systems (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, I = 0.1 M by NaCl, 0.05 mmol HCl).

More stable Hg^{2+} complexes usually take place with S-donor ligands.[26] The Hg^{2+}–HPT complex was considered in this study to reveal the extent of the coordination properties of the HPT. HPT, as a hard base, is not expected to fully interact with the soft acid Hg^{2+}.[27,28] However, the fact is Hg^{2+} forms a reasonably stable diversity of complexes with HPT. Species distribution curves for the Hg–HPT systems and behaviors of HPT in the presence of Hg^{2+} (1:1, ML complex form) are given Figures 6 and 7, respectively.
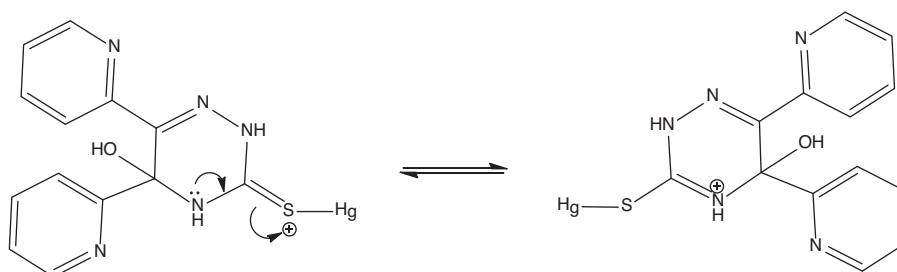

Figure 7. Behavior of HPT in the presence of Hg^{2+}.

A variety of species were formed in solution at pH 3–10. The HgH_2L and HgL species were formed in the acidic and basic medium, respectively. The main species, HgHL, formed in the range pH 4 up to 10 and its maximum availability of 90% was in the neutral area of pH 7. Hydrolyzed species developed in this solution at pH 8.5 and reached their highest level at over pH 10.

Figure 8 shows all the species that existed in the Cu^{2+}–HPT system between pH 5 and 11. The main complexes existing in the solution are CuHL and CuL and the complexes existed in the range pH 6–10.5. At a pH of about 8, approximately 65% of the total Cu^{2+} turned to CuHL, forming the main constituent of the complex species. CuL formed about 70% of the total Cu^{2+}, which revealed its maximum occurrence at a pH of about 9.5, while the maximum occurrence of CuH_2L (just less than 20%) was at a pH of about 6.5. The final species that existed in the case of the Cu^{2+}–HPT complex was $MH_{-2}L$ (hydrolyzed species), which occurred in an appreciable amount at a pH above 11, approximately 99% of the total Cu^{2+}.
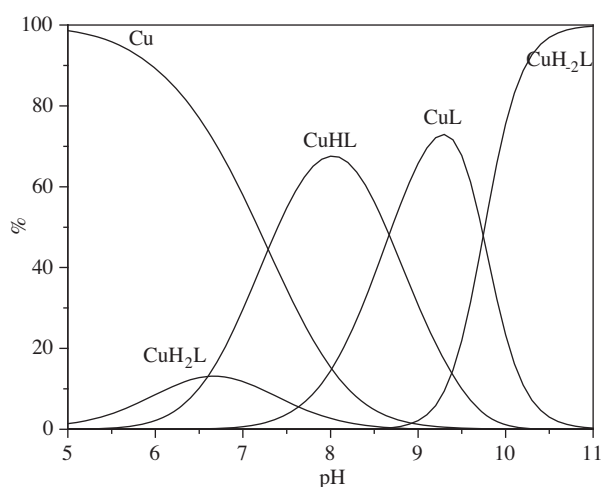
Figure 8. Species distribution curves for the Cu–HPT systems (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, I = 0.1 M by NaCl, 0.05 mmol HCl).
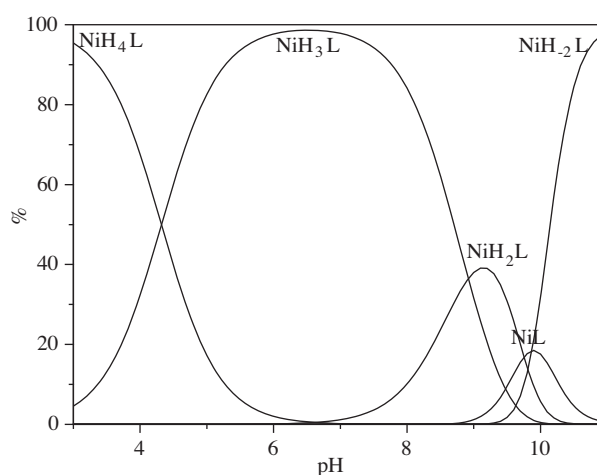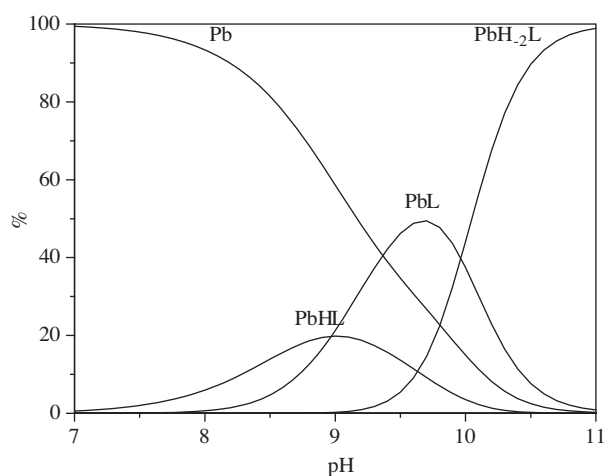
Figure 9. Species distribution curves for the Ni–HPT systems (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, I = 0.1 M by NaCl, 0.05 mmol HCl).

According to Figure 9, a variety of Ni^{2+}–HPT complexes were formed in solution at a wide range of pH values. Four different species exist within the pH area span of pH 3 up to just above 11. NiH_4L is almost the only species formed in the acidic region, approximately 90% up to pH 3. The main complex existing in the solution is NiH_3L and the complex existed in the range pH 3 up to 10. At a pH of about 7, approximately 99% of the total Ni^{2+} turned to NiH_3L, forming the main constituent of the complex species. The other species present in addition to the above-mentioned is NiH_2L, which forms about 40% at pH 9, while the maximum occurrence of NiL (just less than 20%) was at a pH of about 10. The $NiH_{-2}L$ (98%) is the final species, which was formed above pH 11.

Pb^{2+} can adopt many different geometries in its complexes, allowing a degree of tolerance for ligand configuration that is not seen, for example, in d-block elements, coupled with the ability to bind well to both hard and soft donor atoms.[19] However, in this study, stable Pb–HPT complex was not obtained. According to Figure 10, the main complexes existing in the solution are PbHL and PbL and the complexes existed in the range pH 7 up to 11. At about the pH of 9, approximately 20% of the total Pb^{2+} turned to PbHL, forming the main constituent of the complex species. PbL formed about 50% of the total Pb^{2+}, which revealed its

maximum occurrence at a pH of about 9.8. Hydrolyzed species developed in this solution at pH 9 and reached their highest level at over pH 11.


Figure 10. Species distribution curves for the Pb–HPT systems (0.01 mmol HPT, 20% ethanol–water mixed, 25.0 ± 0.1 °C, $I = 0.1$ M by NaCl, 0.05 mmol HCl).
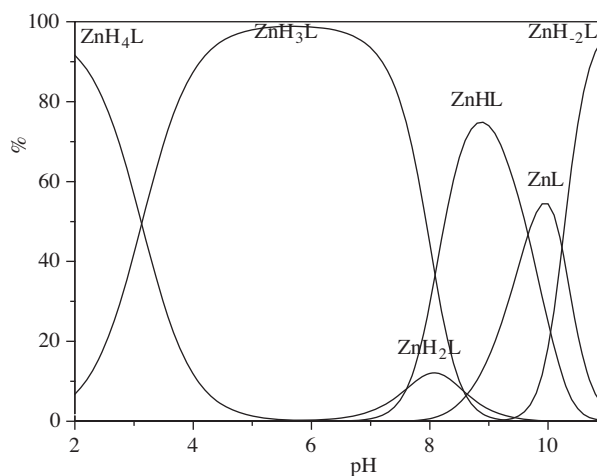
Figure 11. Species distribution curves for the Zn-HPT systems (0.01 mmol HPT, 20% ethanol-water mixed, 25.0 ± 0.1 °C, $I = 0.1$ M by NaCl, 0.05 mmol HCl).

Figure 11 shows Zn^{2+}–HPT complexes species started to exist at even lower pH values than other complexes; ZnH_4L existed in the solution at a maximum amount of about 90% at pH 2. The main complex existing in the solution was ZnH_3L and the complex existed in the range between pH 2 up to pH 9. At about pH 6, approximately 99% of the total Zn^{+2} turned to ZnH_3L, forming the main constituent of the complex species. The other species were ZnL, which forms about 50% at pH 10, and $ZnHL$, which formed about 70% at pH 9; the maximum occurrence of ZnH_2L (just less than 20%) was at a pH of about 8. The final species that existed in the case of the Zn^{2+}–HPT complex was $ZnH_{-2}L$ (hydrolyzed species), which occurred in an appreciable amount at a pH above 11, approximately 99% of the total Zn^{2+}.
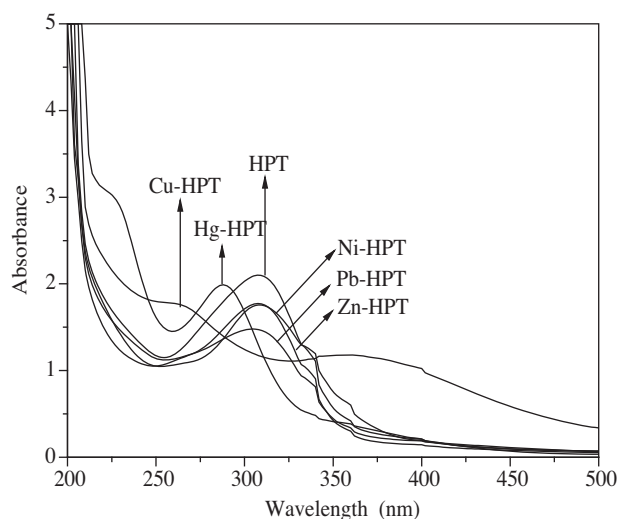
Figure 12. Absorbance spectra of M–HPT.

The wavelength of maximum absorption was determined using a UV spectrophotometer for each metal at the appropriate pH. The differences in the complex between Hg and ligand were found clearly (Figure 12). Maximum absorption was obtained at 320 nm for HPT, Ni–HPT, Pb–HPT, and Zn–HPT, but some shifts in the maximum absorption wavelengths of Cu–HPT and Hg–HPT were observed variously. While these shifts formed as a shoulder type peak for Cu–HPT, they formed as an obvious peak for Hg–HPT at 286 nm. This peak showed that there is a strong and stable complex between Hg and HPT, and the findings were supported by the potentiometric results.

The same ratio was obtained between Hg^{2+} and similar ligands in the literature spectrophotometrically. In this literature, a new sensitive and selective fluorescent sensor for Hg^{2+} was formed with a similar ligand.[29] Therefore, this work is supported by the literature results.

4. Conclusions

The deprotonation constant (pK_a) values were 9.69, 9.23, 6.30, and 3.58 for HPT in acidic medium. When the solution including Hg^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} and the ligand and at 1:1 ratio were titrated with the alkali, various complexes $(MH_4L–ML)$ occurred. The more stable complexes were formed between M^{2+} and HPT in the bases ML species. Their magnitude was in the following order: Hg > Cu > Zn > Pb > Ni for the complex ML type. According to potentiometric and spectrophotometric results, the HPT and Hg^{2+} combination formed a selective and highly stable complex at pH 7.

Acknowledgments

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