Original Article

Spectrophotometric Study of Complications Reaction of N, N’-Adipylbis (5-phenylazo salicylaldehyde hydrazone) with a Variety of Metal Ions in Methanol Solution

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ABSTRACT

Spectrophotometric studies prior to construction of ISE is very necessary step, and Selective and simple determination of elements via Ion Selective Electrodes (ISE) are very attractive in chemical analysis.

In order to obtaining the new ISE for determination of La^{3+} ions, the interaction of N, N'-adipylbis (5-phenylazo salicylaldehyde hydrazone (L) with different trivalent and divalent metal ions, investigated, the complexation of L with Cr^{3+}, Al^{3+}, Ce^{3+}, Gd^{3+}, Yb^{3+} and La^{3+} ions and also Ni^{2+}, Cu^{2+}, ions in acetonitrile solution are studied spectrophotometrically, and confirmed by conductometric, NMR and IR studies.

It was found that in the studied trivalent metal ions, 1:1 complexes were formed in solution. In the case of divalent metal ions both ML and M_2L complexes were formed. The K_f Values of the resulting complexes between ligand and different metal ions were evaluated by computer processing of the corresponding mole ratio data to an equation that derived former using a non-linear curve-fitting program, KINFIT. The resulting K_f values for all metal ion complexes studied showed that the stability of the complexes studied varies in the order of: $La^{3+} > Yb^{3+} > Ce^{3+} > Gd^{3+} > Al^{3+} > Cr^{3+}$.

The results revealed that this ligand is candidate for construction of new ISE for simple and selective determination of La^{3+} ions.

Keywords: ISE, Spectrophotometric metal ions, N, N’-Adipylbis (5-phenylazo salicylaldehyde hydrazone).

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INTRODUCTION

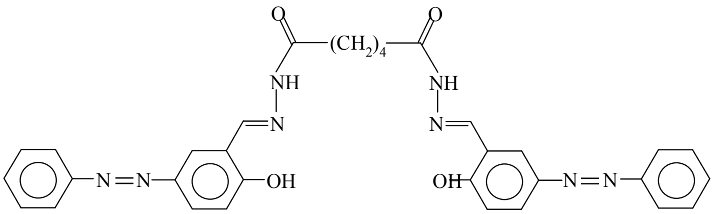
Due to widespread industrial and biological use of lanthanum[1-3], its selective determination is of critical importance. Lanthanum compounds are extensively used in making of optical glasses, gasoline-cracking catalysts, polishing compounds and carbon arcs, and in the iron and steel industries to eliminate sulfur, carbon and some other electronegative elements from steel and iron alloys[1,3]. Recently, attempts were made to promote germination of natural rice seed by treating them with lanthanum nitrate[4]. Using Lanthanum chloride in rice root membranes appears some changes in lipid peroxidation, and ATPase activities of plasma[5].

The previously methods for trace analysis of lanthanum and other lanthanide elements in solution include X-ray fluorescence[6], isotope dilution mass spectrometry [7], neutron activation analysis [8], ICP-MS[9], ICP-AES[10] and spectrophotometry[11]. But, these methods are not only time consuming, but also involving sample manipulations, or too expensive for most analytical laboratories. Then, introducing of new ion-selective electrodes for lanthanum (III) is very interesting[12-17].

In the past decayed, a variety of ionophor compounds inclode acyclic and macrocyclic ligands is used for instruction of new ion-selective electrodes for a number of trivalent metal ions including Fe^{3+} [18], Cr^{3+} [19], Ce^{3+} [20], La^{3+} [13], Yb^{3+} [21], Gd^{3+} [22], Sm^{3+} [23]and Nd^{3+} [24] have been used. In the presence work the intraction between N, N'-adipylbis (5-phenylazo-salisylaldehyde hydrazone) (L) and some metal ions were studied and confirmed that the ligand (L) is a interesting neutral ionophore for the preparation of a PVC-based polymeric membrane electrode with a good results for selective determination of lanthanum(III) ion.

EXPERIMENTAL

Reagent grade metal nitrates and TEAP (All from Merck) and recently synthesized 2, 2' – [1, 2 – panthandiyl bis (nitrilopanthylidyne)] bis (1- naphthalene) were of highest purity accessible and was used without any more purification exclude vacuum drying over P_2O_5 [27].



(L)

Spectroscopic grade methanol (from Aldrich) were purified and dried by the previously described method and used.

All UV/vis. Spectra were recorded on a computerized HP Agilent 8453 instrument equipped with a HUBER polystate temperature controller using a 10 mm quartz cell.

RESULTS AND DISCUSSION

In order to obtain some information about the stoichiometry, stability and selectivity of the ligand **(L)** for its complexes with different trivalent and divalent metal ions, we investigated the complexation of L with Cr^{3+}, Al^{3+}, Ce^{3+}, Gd^{3+}, Yb^{3+}, La^{3+}, Ni^{2+}, and Cu^{2+} ions in methanol solutions spectrophotometrically. It was found that addition of metal ions to a 1.88×10^{-5} M solution of L in the presence of 1.0×10^{-2} M of TEAP, added as a supporting electrolyte to maintain the ionic strength of solution during titration, results in a considerable change in absorption spectrum of the L. Sample electronic absorbtion spectra for the titration of L without and in the presence of increasing amounts of La^{3+} ion are presented in Fig.1. As can be seen, the complexation was accompanied by a relatively strong shift of the absorption band of L, with two λ_{max} at 296.7 and 344.3 nm in methanol solution, toward a longer wavelength (i.e., λ_{max} = 386.9 nm), through a sharp point at 362.3 nm. Such illustration affect on the electronic spectra of L must be in relation to a large change in the conjugation of the ligand molecule due to its complexation with La^{3+} ion. (See figure 1-3.)

The absorbance vs. $[M^{3+}]/[L]$ mole ratio plots gotten at the λ_{max} of various amounts of M^{3+}-L complexes are presented in Fig. 2. As it is obvious, in the case of all trivalent metal ions examined, the absorbance-mole ratio plots revealed a sharp inflection point at a $[M^{3+}]/[L]$ mole ratio of about one, confirming the formation of a 1:1 complex in solution. It is interesting to note the sharpness of the inflection point changed clearly with the nature of M^{3+} ions used, which is obviously an indication of a change in stability of the resulting complexes; i.e., the sharper the inflection point, the more stable the resulting 1:1 complex.

The formation constants of the resulting 1:1 complexes between L and different M^{3+} ions were evaluated by computer fitting of the corresponding mole ratio data to an equation that derived earlier [25] using a non-linear curve-fitting program, KINFIT[26]. A sample computer fitted curve for complexa formation of L with La^{3+} ions is exhibited in Fig. 3. The resulting K_f values for all metal ion complexes studied are summarized in Table 1. As is obvious from Table 2.1, the stability of the complexes studied varies in the order $La^{3+} > Yb^{3+} > Ce^{3+} > Gd^{3+} > Al^{3+} > Cr^{3+}$.

The interaction of ligand **(L)** with Ni^{2+} and Cu^{2+} ions were also investigated in this work. The absorption spectra and the related mole ratio plot for interaction of ligand in the presence of increasing metal ion concentrations are exhibited in Figures 4 and 5.

As it is obvious from these two figures, in the case of Ni^{2+} and Cu^{2+} ions, the corresponding absorbance-mole ratio plots show two distinct inflection points at the metal ion-to-ligand mole ratios of about 1 and 2, indicating the successive formation of 1:1 and 2:1 M_2L complexes in methanol solution. The reason for this evidence may be due to the ligand structure (L), the ligand is a multidentate chelating ligand, and then it binds the trivalent metal ions through all eight coordination positions. But in the case of divalent ions such as Ni^{2+} and Cu^{2+}, the stoichiometry maybe M_2L as well as ML to coordinate the metal ions properly and occupy all coordination sites.

The K_f values of the formatted complexes between L and different M^{2+} ions were computed by computer fitting of the related mole ratio data to a previously derived equation[25] applying a non-linear curve-fitting program, KINFIT[26]. Two computer fitted curves for complexation of L with Ni^{2+} and Cu^{2+} ions are shown in Fig. 2.6. The resulting K_f values for all metal ion complexes studied are also summarized in Table 1. (See figure 4-6.)

The conductometric studies were carried out and the results (not included here) confirmed above mentioned stoichiometries.

To have better understanding of the complex formation reaction the NMR an IR spectrum of the L in presence and absence of cations separately investigated (not included too), and chemical shifts and shift in wave numbers clearly showed the complex formation in the solution.

To study the composition of complexes, the continuous variation method was performed[28-31]. In the case of continues variation method known as job's method a series of solutions is prepared that the total moles of metal and ligand n_{tot}, in each solution are the same. Thus two mother solutions of the metal and ligand were prepared and mixed with different volume fractions to reach different mole fractions. Then the absorbances of the solutions were measured at λ_{max}. Typically the resulting corrected absorbance vs. X_{Yb} plot for a trivalent metal ion is shown in Fig. 7. As seen from Fig. 7, the plot possesses only one inflection point at X_{Yb} of 0.5, clearly supporting the formation of 1:1 Yb-L (ML) type complex in the solution. (See figure 7.)

CONCLUSION

In this work, interaction of N, N'-adipylbis (5-phenylazo salicylaldehyde hydrazone (L) with different trivalent and divalent metal ions, investigated. The complex formation of L with Cr^{3+}, Al^{3+}, Ce^{3+}, Gd^{3+}, $Yb^{3+}$and La^{3+} ions and also Ni^{2+}, Cu^{2+} in methanol solution were studied spectrophotometrically and confirmed by NMR and IR spectroscopies and conductometric too.

Results clearly revealed that L is very selective for M ions and is suitable for an ion selective electrode ISE for determination of this caution.

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Table 1. The K_f values of M^{n+}-L complexes in methanol solution at 25 °C

Cation	Log K_f	Log K_2
La^{3+}	5.87 ± 0.04	-
Yb^{3+}	5.04 ± 0.06	-
Ce^{3+}	4.8 ± 0.03	-
Gd^{3+}	3.2 ± 0.04	-
Al^{3+}	2.5 ± 0.02	-
Cr^{3+}	< 2	-
Cu^{2+}	3.8± 0.02	4.02± 0.03
Ni^{2+}	4.8± 0.04	3.6± 0.02

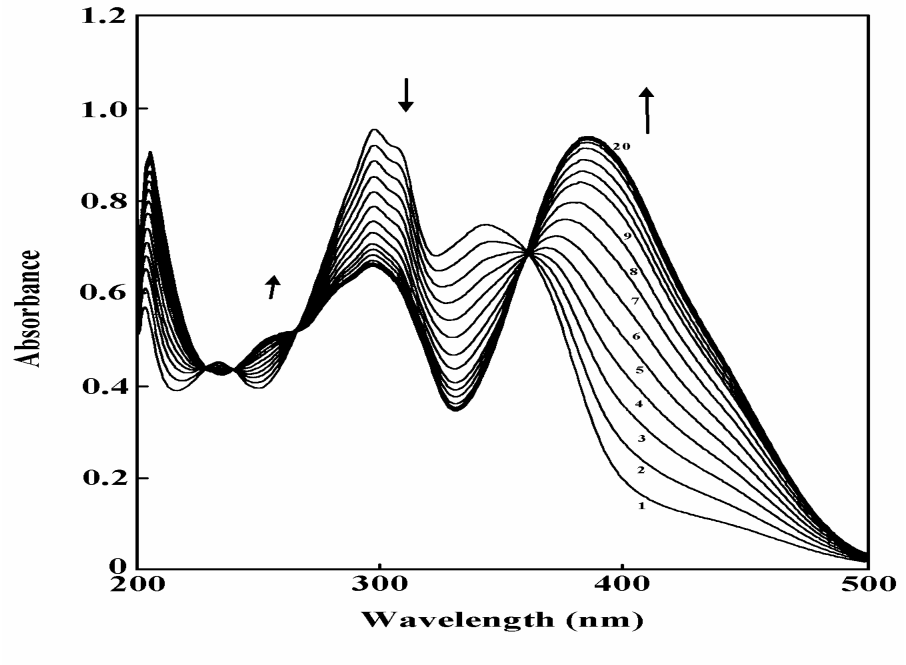
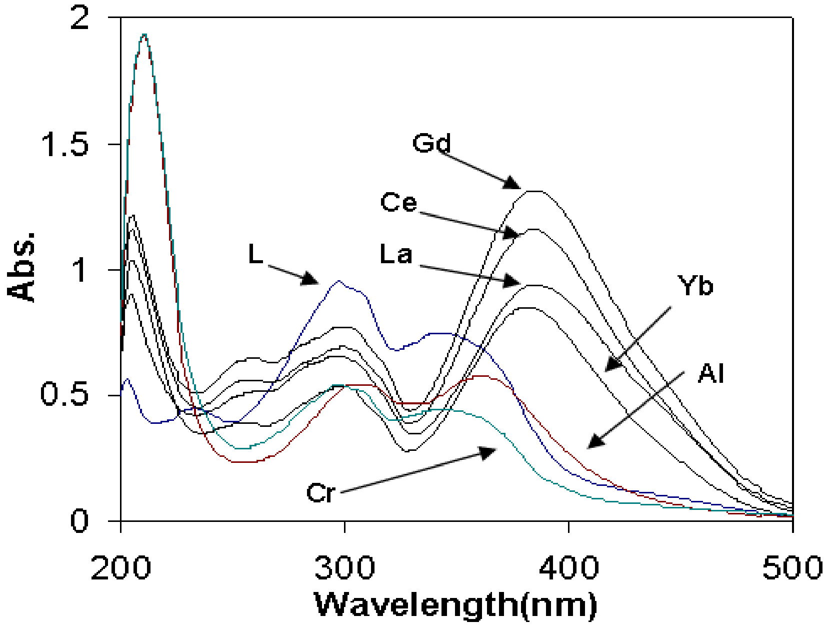


Figure 1. Electronic spectra of a 1.88 × 10^{-5} M solution of L in methanol in the presence of increasing amounts of La^{3+}.[La^{3+}]/[L] mole ratios are: (1) 0, (2) 0.065,(3) 0.13, (4) 0.195, (5) 0.26, (6) 0.32, (7) 0.39, (8) 0.46, (9) 0.52, (10) 0.59, (11) 0.65, (12) 0.78, (13) 0.95, (14) 1.1, (15) 1.3, (16) 1.5, (17) 1.7, (18) 1.9, (19) 2.2, (20) 2.5



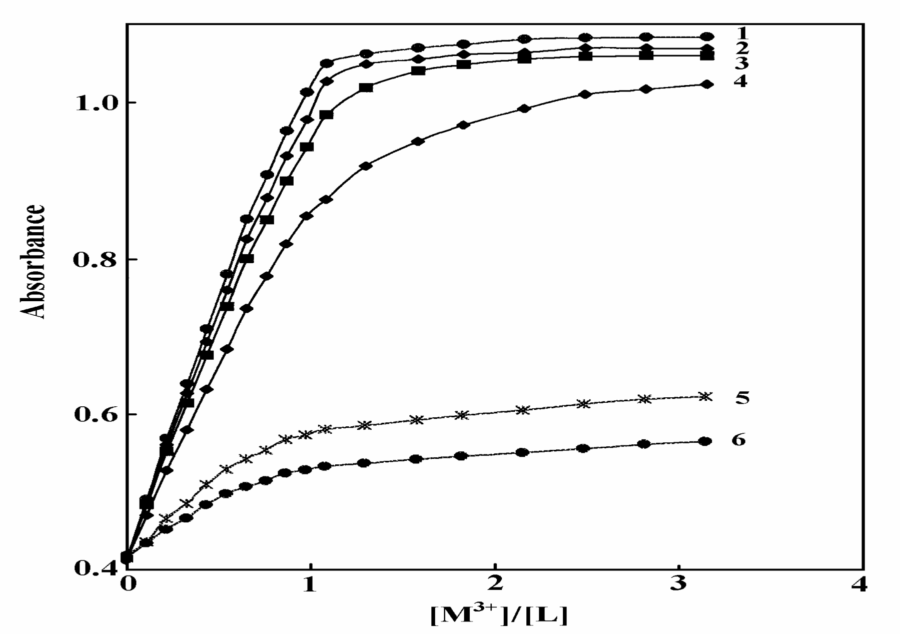


Figure 2. Absorbance vs. $[M^{3+}]/[L]$ molar ratio plots for different M^{3+} metal ions in methanol solution: (1) La^{3+}, (2) Yb^{3+}, (3) Ce^{3+}, (4) Gd^{3+}, (5) Al^{3+} and (6) Cr^{3+}

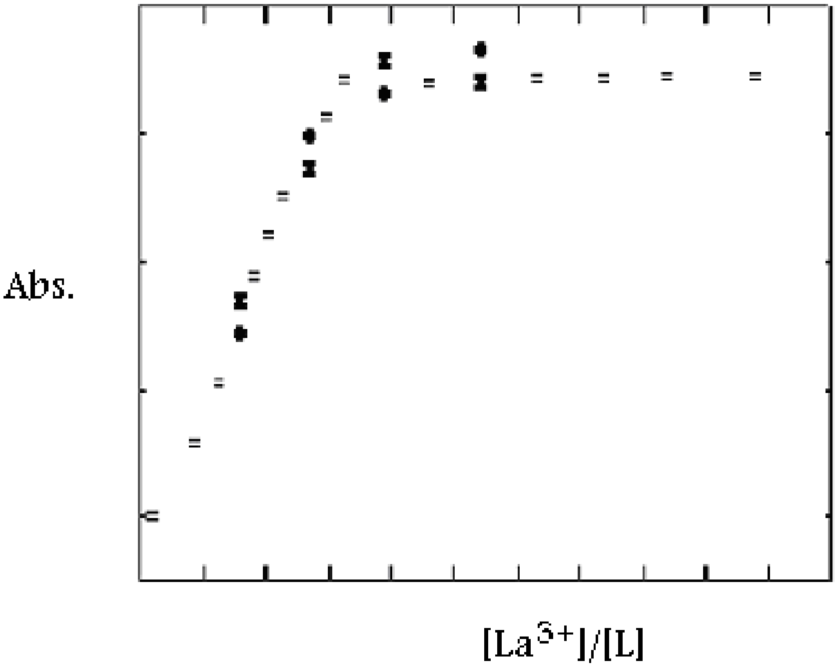


Figure 3. Computer-fitted curve for complexation of L with La^{3+} ions (Fig.2.2). Points (o), (×) and (=) indicate theoretical, experimental and good agreement between theoretical and experimental points, respectively

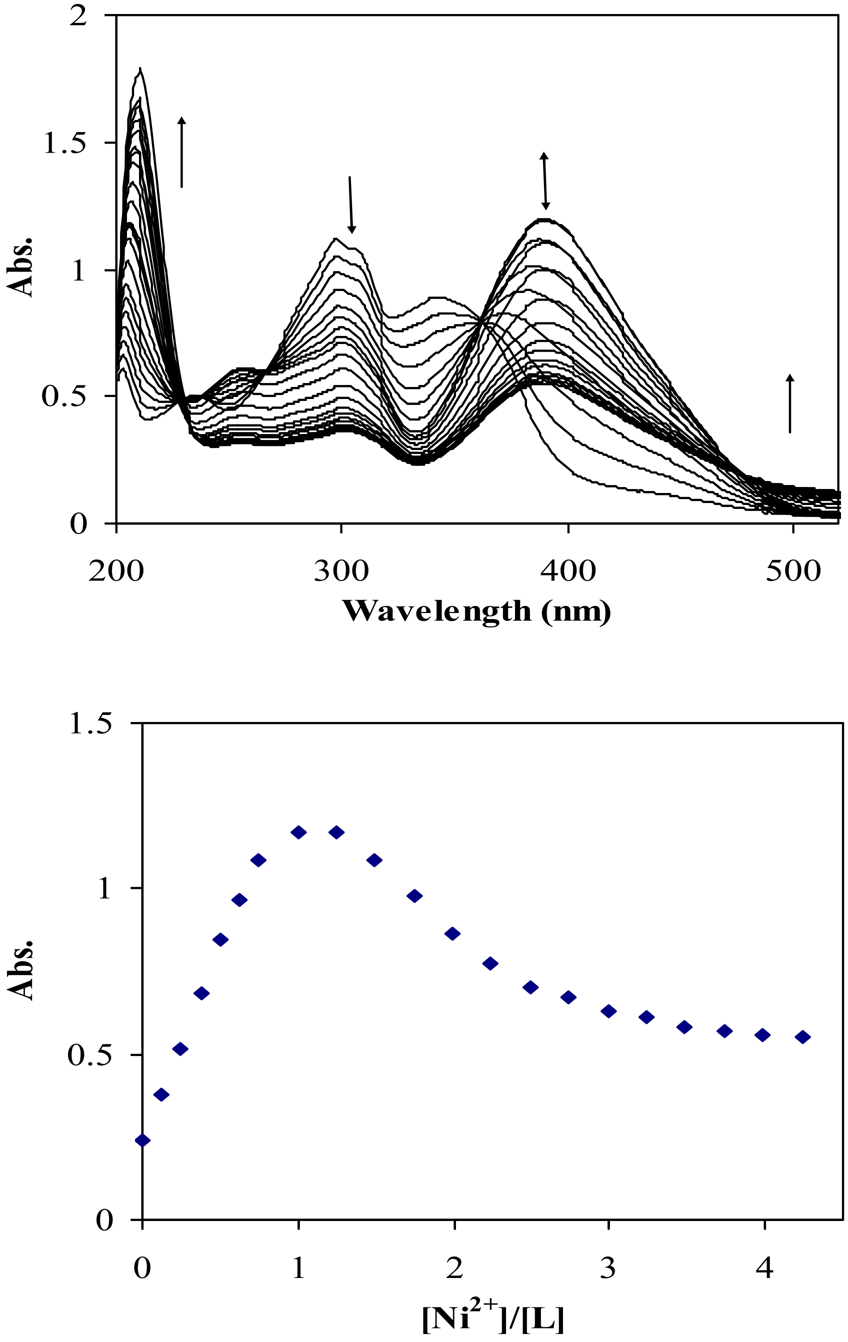


Figure 4. A) Electronic spectra of a 1.876× 10^{-5} M solution of L in methanol in the presence of increasing amounts of Ni^{2+} from a $[Ni^{2+}]/[L]$ molar ratio of 0.0 to 4.2. (At 25°C and TEAP=0.01M). **B)** The corresponding abs. vs. $[Ni^{2+}]/[L]$ plot in 397 nm

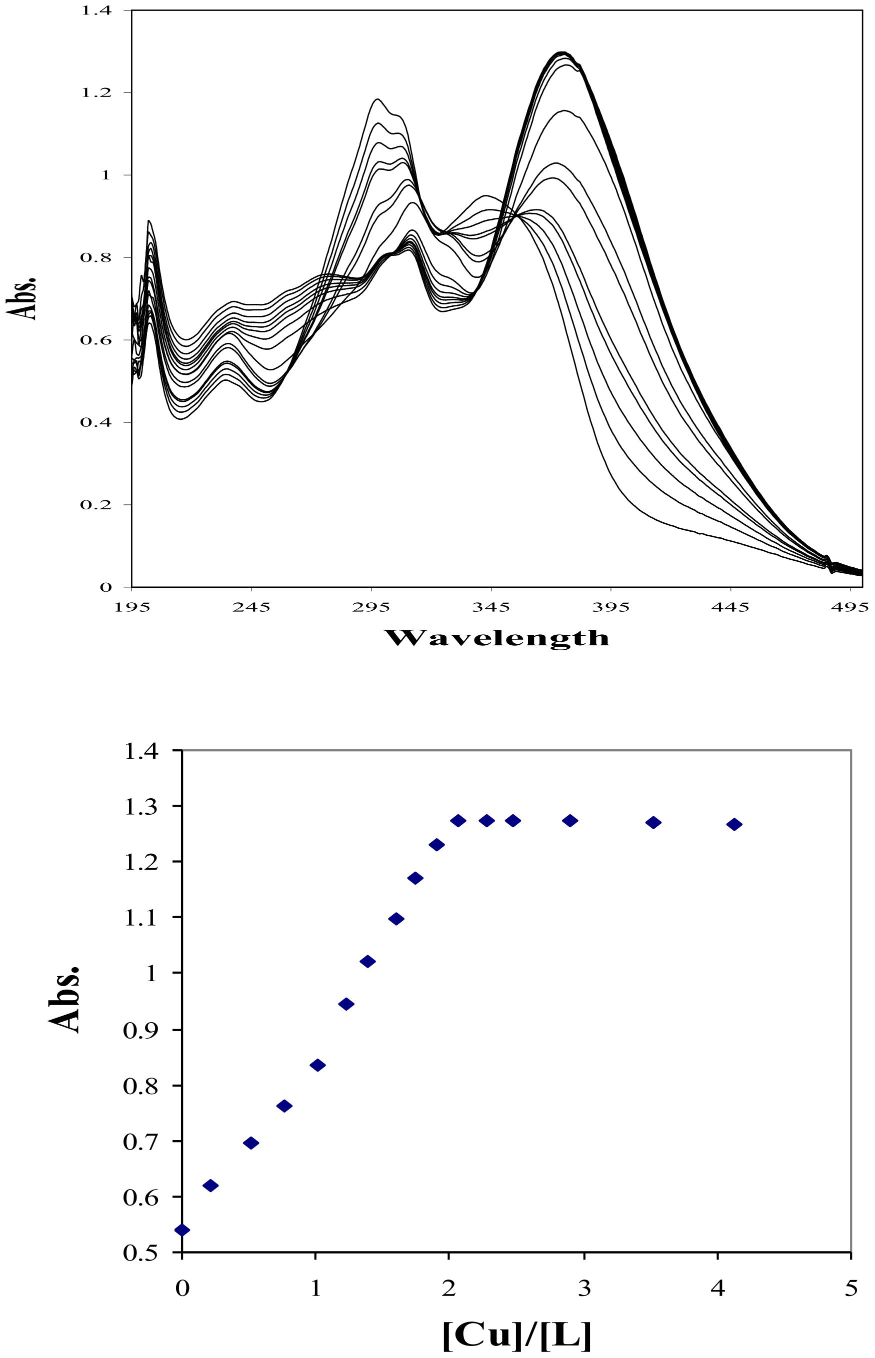


Figure 5. A) Electronic spectra of a (1.876× 10^{-5} M) solution of L in methanol in the presence of increasing amounts of Cu^{2+} from a [Cu^{2+}]/[L] molar ratio of 0.0 to 4.1. (At 25°C and TEAP=0.01M), **B)** the corresponding abs. vs. [Cu^{2+}]/[L] plot in 380 nm

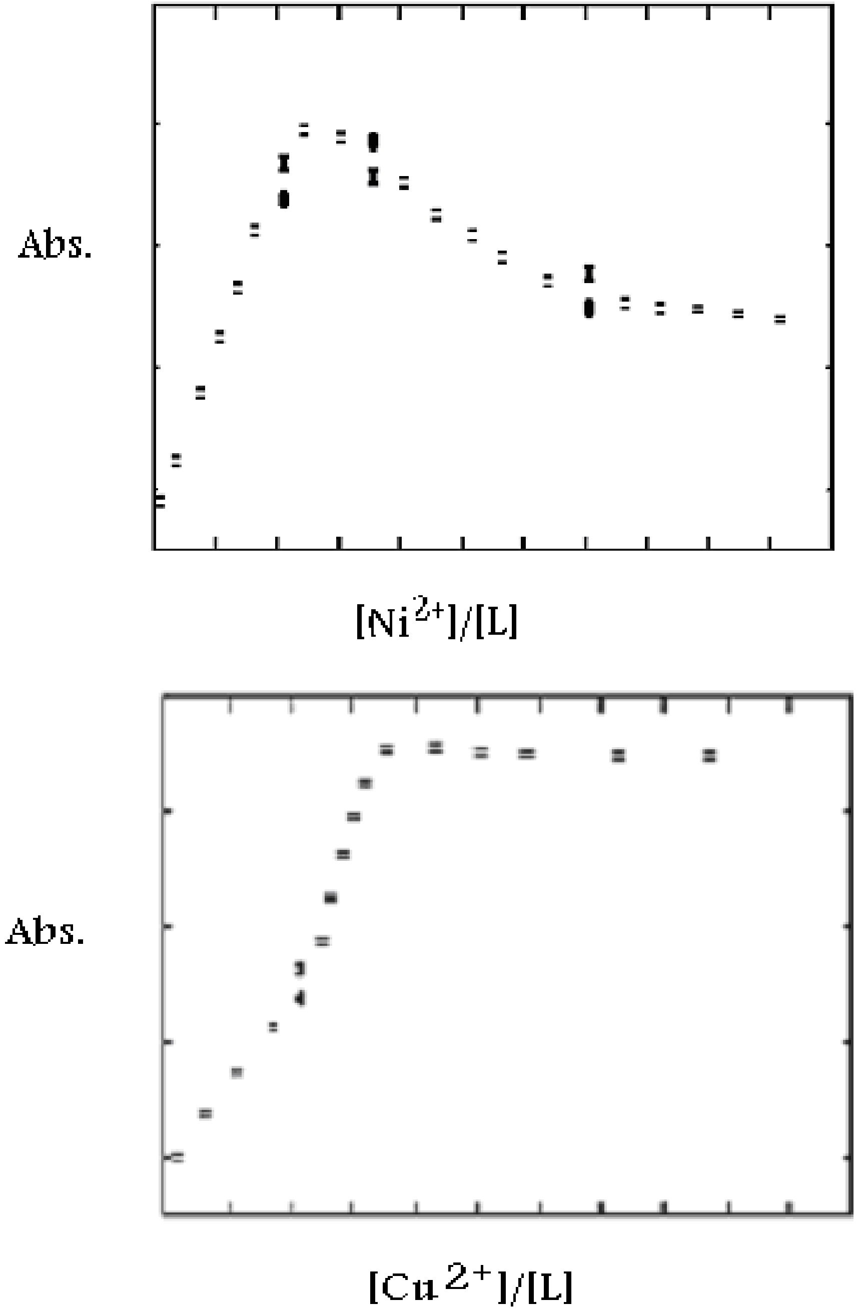


Figure 6. Computer-fitted curves for complexation of L with Ni^{2+}(A) and Cu^{2+}ions (B); (Figures 2.4-5), (×) experimental points, (o) calculated points, and (=) the experimental and calculated points are the same within the experimental error

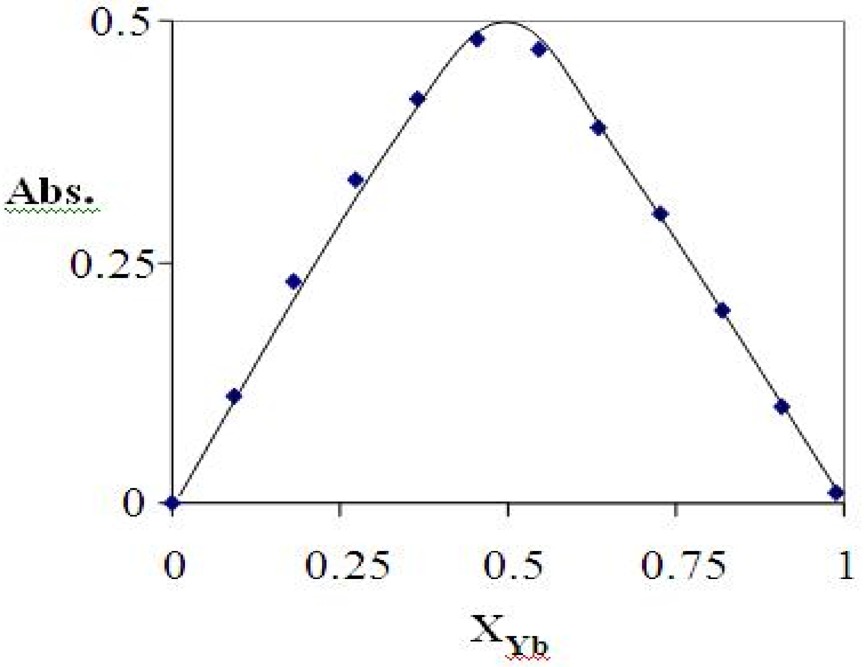


Figure 7. Continuous variation plot for L-Yb system in metanol solution (λ_{max}=380 nm)