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Original Research Article

Complex Formation of Bis(salicylidene)ethylenediamine (Salen type ligand) with Cupper(II) Ions in Different Solvents: Spectrophotometric and Conductometric Study

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ABSTRACT

The complexation reaction between salen (Bis(salicylidene)ethylenediamine) and Cu(II) cations in methanol (MeOH), 2-propanol (2-PrOH), acetonitrile (AN), tetrahydrofuran (THF), and chloroform (CHCl₃) as nonaqueous solvents at 25° C has been investigated. The stoichiometry and formation constants of complexes have been determined spectrophotometrically and conductometrically by method of continuous variations and mole ration method. The stoichiometry of Cu(II)-salen complexes in all solvents were 1:1 (ML) type using the two methods. By method of continuous variation, chloroform > 2-propanol > methanol ~ acetonitrile ~ tetrahydrofuran. However, by mole ratio method, the order of stability was as follows: chloroform ~ tetrahydrofuran > 2-propanol > methanol ~ acetonitrile. The resulting average of pK_f values in each solvent using the two spectrophotometric methods was as follows: 7.40, 6.89, 6.8, 6.22, and 6.18 for chloroform, 2-propanol, tetrahydrofuran, acetonitrile, and methanol, respectively. The Cu(II) cation formed a more stable complex with salen in chloroform. However, the less stable complex was in methanol.

Keywords: Copper, Conductometry, Salen, Schiff base, Spectrophotometry.

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Introduction

Schiff bases acquire a significant deal of interest in several fields of chemistry including analytical chemistry, inorganic biochemistry, coordination chemistry, supramolecular chemistry and catalysis [1-5]. Among the schiff bases, Salen-types, which produced from salicylaldehyde and diamines, are valuable type of organic compounds due to the ease with which they can be synthesized, their fascinating structural flexibility, diverse properties and their superb chelating power to make transition metal complexes. Generally, Salen –type of schiff base performs as a tetradentate chelating ligand through two covalent and two coordinate covalent sites located in a planar array to generate stable mononuclear complexes [6]. This type of coordination presents the Salen ligand typical for the equatorial coordination of transition metals, leaving the two axial sites accessible for ancillary ligands [7]. Nevertheless, mononuclear complexes of the Salen-type Schiff base can themselves behave as “complex ligands”, which may be then coordinated via the negatively charged phenoxo groups causing the formation of new multinuclear metal complexes [8].

It is essential to explore metal complexation of N_2O_2 tetradentate Schiff bases compounds in solution and what stability may be assumed because such kind of complexes have been used as biological models to recognize the structures of biomolecules and biological activities [9]. Furthermore, investigating the composition of the complexation reaction in solution is essential in recognizing many processes in analytical, industrial and pollution analyses. Understanding of the equilibrium is similarly essential for explanation of the kinetics of reactions in solution. On the other hand, it is well known that the stoichiometry and complexation of transition metal complexes in solution are clearly affected by the nature of solvent [10]. Solvent molecules themselves may work as coordinating ligands and, thus, coordinate to metal ions in a complex by the displacement of counterions. These displacement reactions strongly rely on the donor capability, dielectric constant, shape, and size of the solvent molecules [11].

Many physicochemical techniques such as spectrophotometric [12], potentiometric [13], conductometric [14], calorimetric [15], polarographic [16] and fluorescence [17] have been employed to examine the stability of transition metal complexes in aqueous and non-aqueous solvents. In our earlier work, we have analyzed the influence of solvents on absorption spectra of pyrazole based ligands and their complexation with some metal ions [18-21].

In the current study, we report the conductometric and spectrophotometric analyses of the stoichiometry, complexation reaction of Salen with Cu(II) in nonaqueous solvents to study the influences of solvent on the complex formation.

Experimental

Reagents

All solvents in the current study were HPLC or spectroscopic grade and used without extra purification. These solvents were methanol (99.9%), isopropanol (99.9%), tetrahydrofuran (99.9%), chloroform (99.9%), and acetonitrile (99.9%). N,N'-Bis(salicylidene)ethylenediamine ligand (indicated in Figure 1) (98%) was obtained from SIGMA-ALDRICH. All chemicals (copper chloride, sodium hydroxide, and 37% hydrochloric acid) were ACS reagent grade and obtained from MERCK. The stock of 1.00×10^{-3} M solutions of salen in five solvents was prepared. The stock of 1.00×10^{-3} M solutions of Cu(II) in deionized water and methanol were also prepared. The Milli-Q water was used in this study.

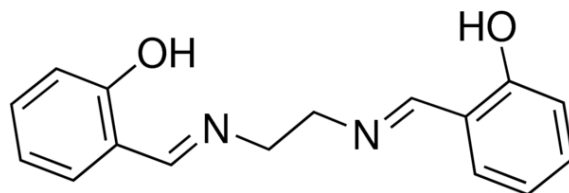


Figure 1. N,N'-Bis(salicylidene)ethylenediamine (salen)

Spectrophotometric Analysis

The UV-VIS absorption spectra were developed using the Agilent Cary 60 UV-Vis Spectrophotometer in the range from 200 to 450 nm. Spectra were recorded at 25°C. To study the effect of solvent on absorption spectrum of Cu-salen complex, a series of diluted solutions (approximately 1.00×10^{-5} M) in each solvent were used.

Complexation Study

Spectroscopy

The absorption maxima of Cu-salen complex in different solvents were investigated by titration of 1.00×10^{-5} M salen solution with 1×10^{-3} M Cu(II) solution (20 μ l additions) and recording the spectrum (from 200 – 450 nm). The complexes just formed were examined for their stability

with time (till 180 min). The stoichiometry and stability constant were determined using method of continuous variation (Job method) [22] and mole ratio method [23].

Conductometry

Conductance measurements were carried out with a Jenway 4510 conductivity meter. A conductivity cell made of quartz was used. The cell constant at 25°C was determined by conductivity measurements of a 0.010 M solution of analytical-grade KCl (Merck) in deionized water. In a typical experiment, 20 mL of Cu(II) ions (5.0×10^{-4} M) was placed in the titration cell, at 25 °C and the conductance of solution was measured. Then, a known volume of a Salen solution (5.0×10^{-3} M) was added in a stepwise mode by a calibrated micropipette. The conductance of the solution was determined after each addition. The Salen solution was incessantly added till the wanted ligand to metal mole ratio was attained.

Results and discussion

Spectroscopic Study

Absorption Spectra of Salen in Different Solvents

The absorption spectra of salen in different solvents and before the addition of Cu(II) ions have been recorded and shown in Figure 2. As displayed, salen displays two absorption maxima, one is sharper and more intense and located at around 260 nm and the other is broader and located at about 320 nm (depending on the solvent). The first one could be attributed to $\pi \rightarrow \pi^*$ transitions and the second should be $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Both the wavelength and intensity of these transitions were affected by the solvent as revealed in Figure 2.

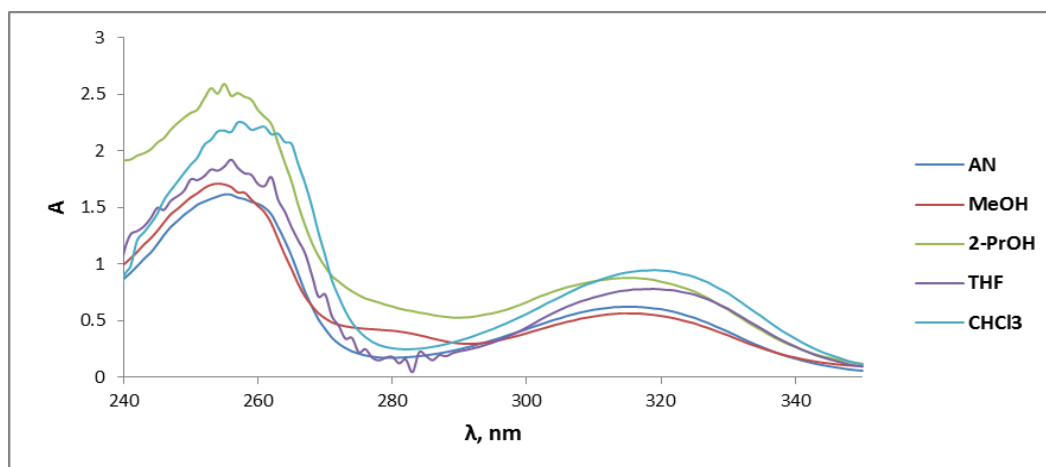


Figure 2. Absorption spectra of salen in different solvents

Complexation of salen with Cu(II) in different solvents

The electronic absorption spectra of Cu(II)-salen complexes in different solvents are shown in Figure 3. The free ligand has an absorption maximum (λ_{\max}) wavelength around 320 nm depending on the solvent. Upon chelating with Cu(II) ions, the absorption maxima (λ_{\max}) were shifted to 358, 356, 366 nm, 367, and 360 in methanol, acetonitrile, tetrahydrofuran, chloroform, and 2-propanol, respectively.

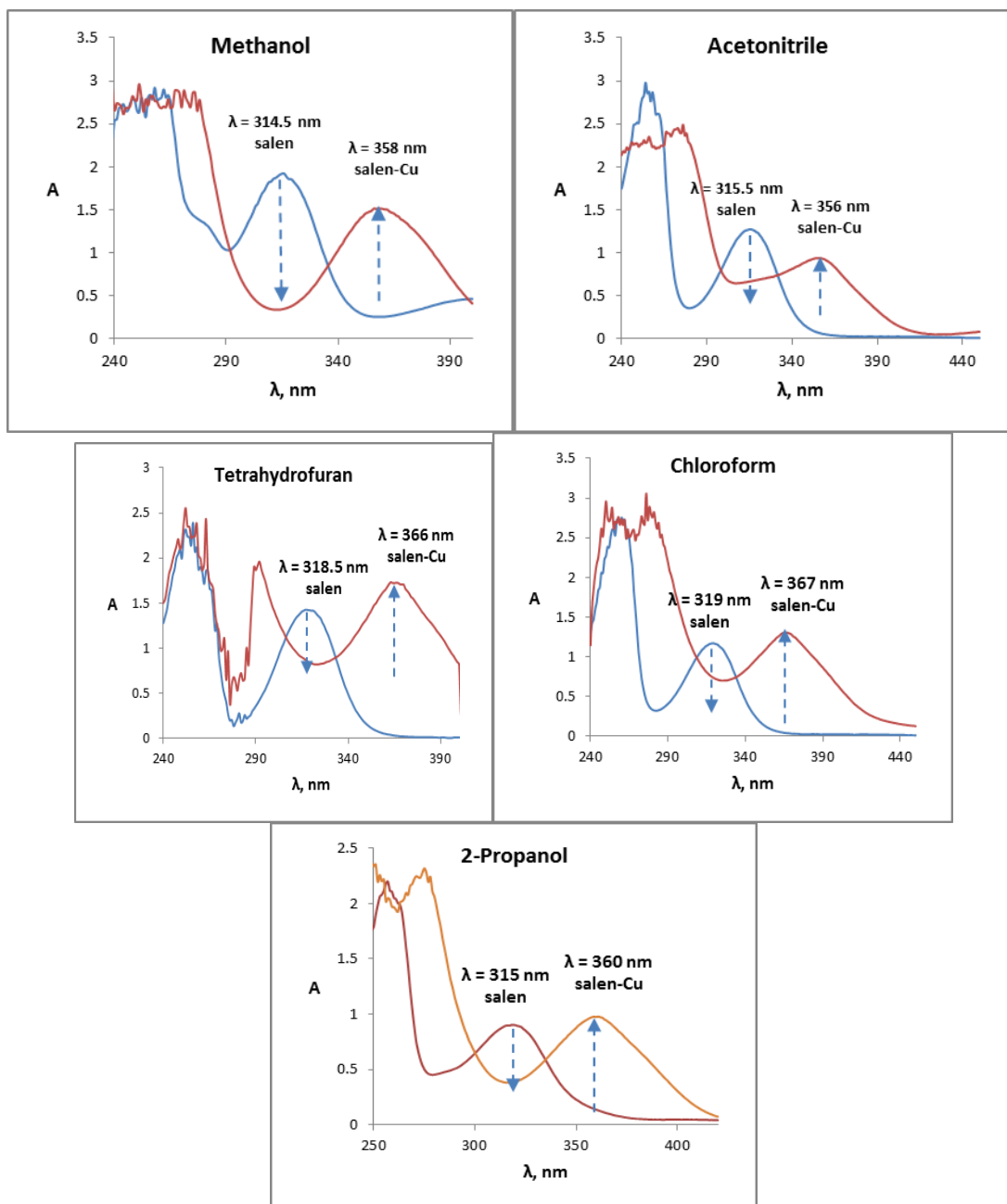


Figure 3. Spectra of free salen and Cu-salen complex in different solvents

The absorption maxima at 320 nm are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. By complexation, the n electrons were used for complexation with Cu(II) and therefore the energy levels n, π , π^* are affected causing the absorption maximum to be shifted. The wavelengths of the absorption maxima of Cu-salen complexes in each solvent are given in Table 1.

Time Effect

The study of the complexes stability with time is an essential parameter since some complexes are not so stable and could dissociate after generation. The two components (metal ion and ligand) are mixed at room temperature, and the absorbance is measured directly. To examine whether the complex being dissociated or still created with time, the absorption of the complex is measured each 15 min and for 180 mins as shown in Figure 4. The absorbance of the complexes remains in all solvents (except in chloroform) stable with time indicating the stability of our complexes. The absorbance of the complex in chloroform is decreased with time indicating the dissociation with the time.

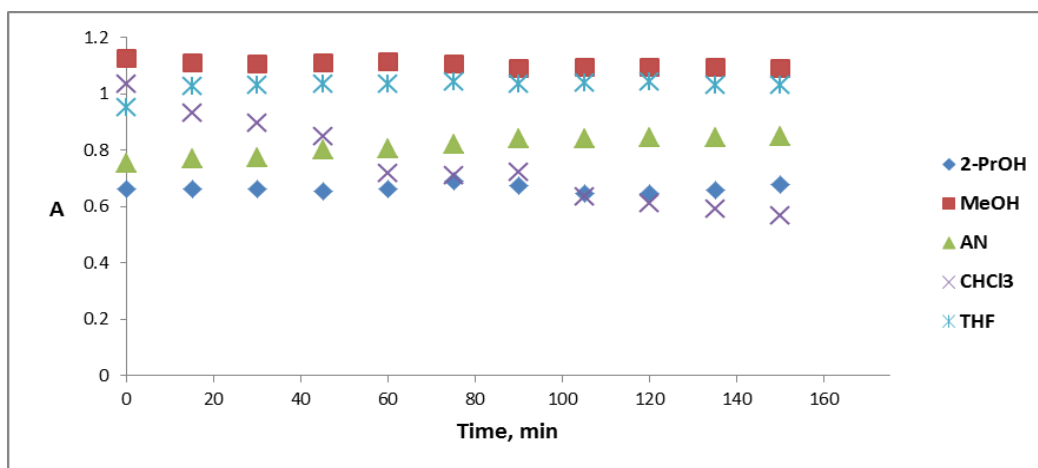


Figure 4. Effect of time on Cu-salen complex in different solvents

The Composition of the Complexes and their Formation Constants (K_f) by Job's Method

The composition of our complexes was determined by the “Job's” method (method of continuous variation). Nine solutions with a final volume of 10 mL were prepared using the same concentration of Cu(II) ions and salen of 1.00×10^{-3} M solutions. Each solution contains different fraction of each constituent. Starting from the first solution which contains 0.10 mL of Cu(II) ions solution and 0.90 mL of salen solution to the final one with 0.90 mL of Cu(II) ions and 0.10 mL of salen solution. The absorbance of each mixture was measured at the appropriate wavelength. These absorbance values for each mixture were plotted against ligand mole fraction and the stoichiometry of each complex was determined. Also, the formation constant of each complex was determined using Job's plot. Job's plot for the complex in each solvent is shown in Figure 5. The molar absorptivity ϵ of the complex can also be determined using Job's method by calculating the concentrations of the complexes at each point and plotting the concentration against the absorbance. The complex stoichiometry, formation constant, and molar absorptivity values are given in Table 1.

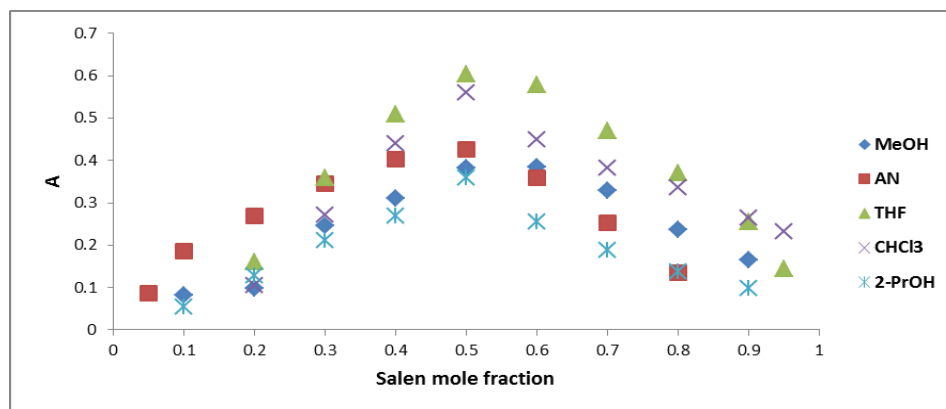


Figure 5. Job's plot of Cu-salen complex in different solvents

Table 1. Cu-salen complexes λ_{\max} , stoichiometry, and formation constant values by Job's Method, Mole Ratio's Method, and Conductometric method

Solvent	λ_{\max} (nm)	m:n	Job's Method			Mole Ratio's Method			Conductometry
			LogK _f	ϵ (L.mol ⁻¹ .cm ⁻¹)	R ²	Log K _f	ϵ (L.mol ⁻¹ .cm ⁻¹)	R ²	LogK _f
MeOH	358	1:1	6.14	7805	0.974	6.21	5130	0.99 1	3.24
2-PrOH	360	1:1	7.02	6970	0.980	6.76	4565	0.99 2	3.50
AN	356	1:1	6.18	9219	0.974	6.25	7065	0.99 7	4.43
THF	366	1:1	6.21	13346	0.980	7.39	14524	0.99 2	3.78
CHCl ₃	367	1:1	7.69	11123	0.989	7.10	15267	0.99 5	6.52

The stoichiometry of all Cu-salen complexes were 1:1 and the stability in each solvent had the following order: Chloroform > 2-propanol > Tetrahydrofuran > Acetonitrile > Methanol

The Composition of the Complexes and their Formation Constants (K_f) by Mole Ratio Method

In the mole-ratio method, a series of solutions is prepared in which the analytical concentration of salen is held constant while that of the copper ion is varied. A plot of absorbance versus mole ratio of the Cu(II) is then prepared. Because the formation constant is reasonably favorable, two straight lines of different slopes that intersect at a mole ratio that corresponds to the combining ratio in the complex are obtained. Typical mole-ratio plots are shown in Figure 6. Formation constants can be evaluated from the data in the curved portion of mole-ratio plots where the reaction is least complete. The complex stoichiometry, formation constant, and molar absorptivity values are given in Table 1. The stoichiometry of all Cu-salen complexes were 1:1 and the stability in each solvent had the following order: Tetrahydrofuran > Chloroform > 2-propanol > Acetonitrile > Methanol

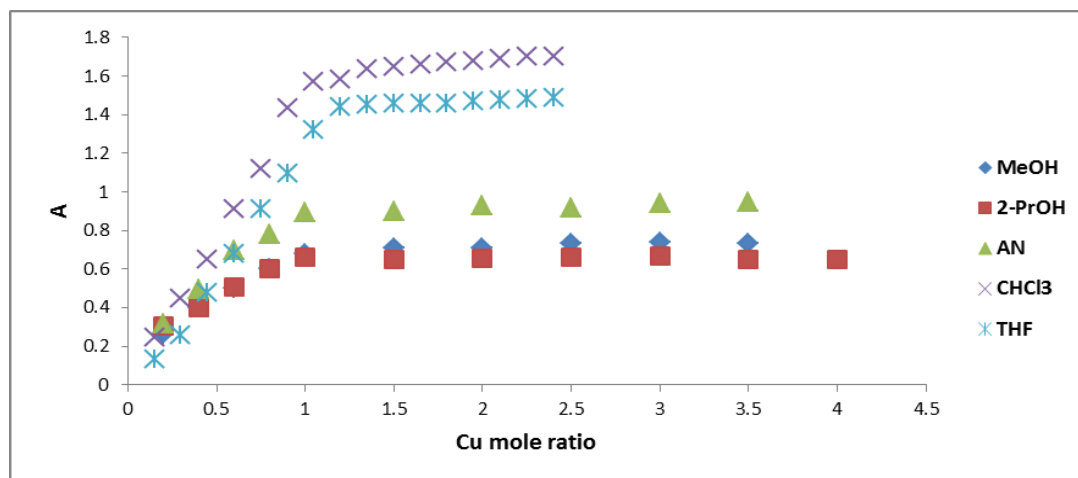


Figure 6. Mole Ratio's plot of Cu-salen complex in different solvents

Conduct metric Studies

The conduct metric methods have been commonly used for determining of formation constants of transition metal complexes [24]. Specifically, conductometric technique provides valuable information regarding the stoichiometry of complexes and affinity of ligands for cations in the solution. The complex formation between Salen ligand and the Cu^{+2} cation in acetonitrile (AN), tetrahydrofuran (THF), methanol (MeOH), 2-propanol (2-PrOH) and chloroform (CHCl_3) was explored by molar conductance variations upon addition of the ligand to the Cu^{+2} ions solution at 25°C . The resultant molar conductance (Λ_M) versus Salen/ Cu^{+2} molar ratio ($[\text{L}]_t/[\text{M}]_t$) are plotted and shown in Figure 7 and 8. As indicated, adding of Salen to $\text{Cu}(\text{II})$ ions in AN, THF, MeOH and 2-PrOH causes the decrease in molar conductance Λ_M values as the $[\text{L}]_t / [\text{M}]_t$ ratio increases. This denotes that the Salen- $\text{Cu}(\text{II})$ complex becomes less mobile than the free solvated Cu^{+2} ions. Conversely, in chloroform, the molar conductance increases with an increase in $[\text{L}]_t / [\text{M}]_t$ ratio, which indicate that the (Salen- Cu^{+2}) complex is more mobile than the solvated Cu^{+2} ions. It is thoroughly recorded that salen complexes have square planar geometry where the metal ion locates in the plane formed by the N_2O_2 donor atoms and solvent molecules coordinate at the two axial positions [25]. It appears that in solvents with N or O donor atoms, the solvent molecules can occupy the axial position of the four-coordinated complex, consequently, the Salen/ Cu^{+2} complex in AN, THF, MeOH and 2-PrOH solvents becomes more bulky and less

mobile. The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots breaks at the point at which the $[L]_t / [M]_t$ mole ratio is approaching one, which indicates the formation of ML complex type in these solvents. The formation constant ($\log K_f$) values in all tested solvents for the Salen/ Cu^{+2} complexes are displayed in Table 1. As indicated, the nature of the solvent has a significant influence on the stability of the resulting complex. The stability constant of Salen/ Cu^{+2} complexes in the examined solvents at 25 °C decreases in the following order: $\text{CHCl}_3 > \text{AN} > \text{THF} > \text{PrOH} > \text{MeOH}$. The attained results disclose that the highest stability of the complex formed in chloroform (the same results obtained using spectroscopic methods). This outcome is consistent with the solvating ability, as expressed by the Guttmann number [26]. In a solvent with a low solvating capability (low donor number), such as CHCl_3 (DN = 6.52), the complex formation tends to be higher, since the solvent weakly solvates the cation and easily be complexed. However, in solvents with higher donicity such as methanol (DN = 30.0), 2-propanol (DN = 30.0), tetrahydrofuran (DN = 20.0) and acetonitrile (DN = 14.1) [26], the rather high solvating ability of these solvents leads to reduce the stability constant, because the solvent competes with the ligand for the cation.

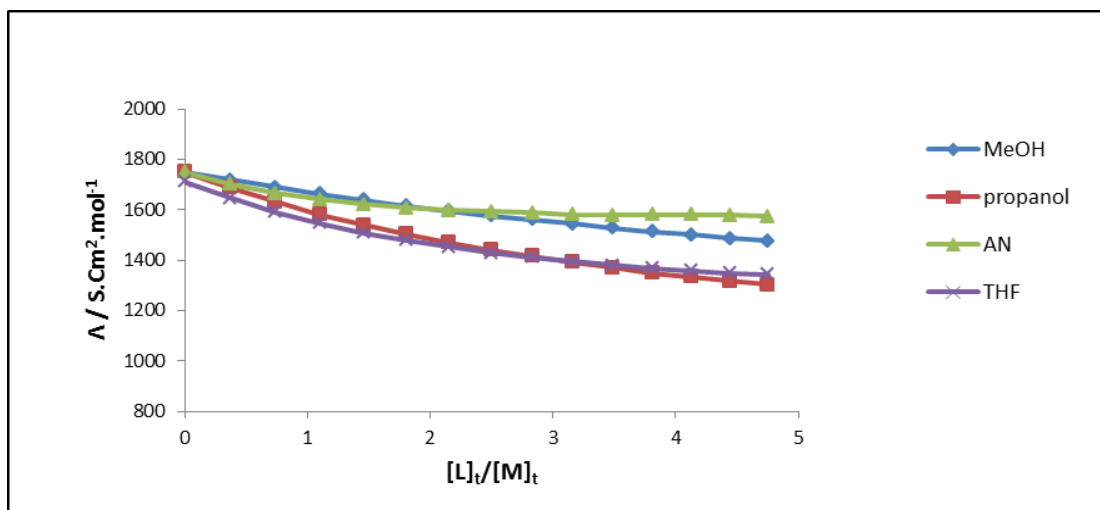


Figure 7. Molar conductivity versus mole ratio plot for the $[\text{Salen}/\text{Cu}^{+2}]$ complex in a MeOH, AN, 2-propanol and THF at 25 °C

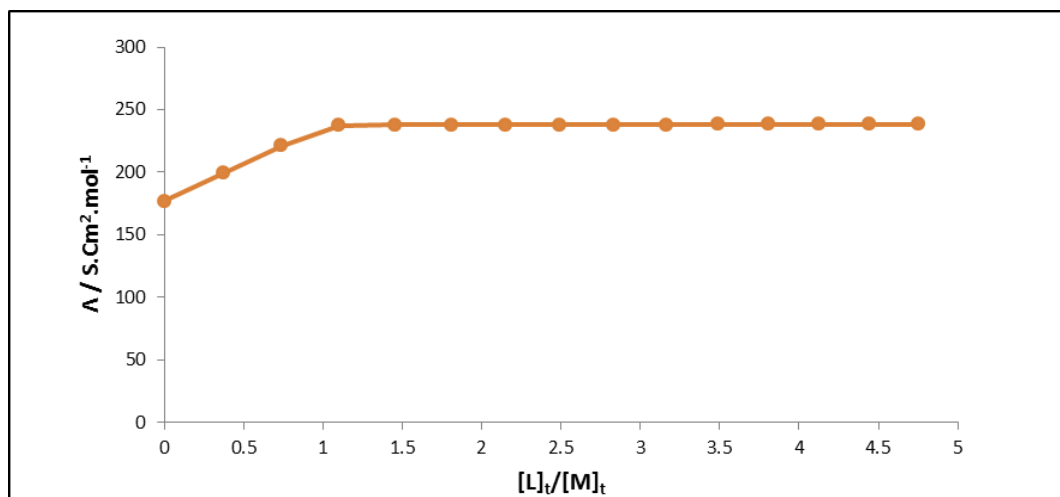


Figure 8. Molar conductivity versus mole ratio plot for the [Salen/Cu²⁺] complex in CHCl₃ at 25 °C

Conclusion

In the present article, a spectrophotometric and conductometric studies were performed to elucidate the complexation between salen (Bis(salicylidene)ethylenediamine) and Cu(II) ions in various non-aqueous solvents. The stability, stoichiometry, and formation constants of formed complexes in each solvent were determined. The resulting complexes possess the stoichiometric ratios of 1:1 (ML) and the formation constant of Cu(II)-salen in chloroform was the highest while in methanol was the least. This because of the Cu(II) ions were less solvated in chloroform and therefore could be easily complexed.

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