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Spectrophotometric and Conductometric Study of Formation Constant and Stoichiometry of Co(II)-Salen Type Ligand Complex

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Abstract

Chelation of Co(II) with N,N-Bis(Salicylidene) ethylenediamine (salen type ligand) have been investigated spectrophotometrically and conductometrically in various solvents (methanol, 2-propanol, acetonitrile, and chloroform). By spectrophotometric measurements, the chelation was performed at 25°C at the wavelengths of the corresponding complex. The stoichiometry of the complexes in each solvent were evaluated using continuous variation method and mole ratio method and the values were found to be 1:1 (M:L). Formation constants (K_f) values were found to be in the order of $10^9 – 10^{10}$ in the examined solvents. The results show there is no significant difference in formation constant values between the complexes formed in the tested solvents. However, the complex formed in chloroform has a slightly larger values of K_f compared to the other solvents. The stability and stoichiometry of the tested complex in MeOH, PrOH, MeCN and $CHCl_3$ at 25°C by conductometric method were also evaluated. Conductometric measurements indicate the formation of (1:1) complexes with stability order: CHCl3 > MeCN > PrOH > MeOH and that was in agreement with the spectrophotometric results. The thermodynamics of the complexation reaction in MeOH was also investigated by conductometric measurements. The stability constant values increase with increasing temperature which means that the complexation reaction is an endothermic process. The negative value of ΔG shows the ability of the Salen ligand to form stable complex with Co(II) and the process trend to proceed spontaneously.

Keywords: Cobalt, Schiff base; Salen, Formation constant, Spectrophotometry.

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1. Introduction

Schiff-bases are considered as a very important class of organic compounds, having wide applications in many biological aspects, proteins, visual pigments, enzymic aldolization and decarboxylation reactions. Moreover, some Schiff's bases and their metal complexes exhibit antibiotic, antiviral and antitumor agents, biological activity. They are also used as catalysts in polymer and dyes industry, beside some uses as antifertility and enzymatic agents [1-5].

A Schiff base or Schiff's base is a type of chemical compounds containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group (R) but not hydrogen. The Schiff base is synonymous with an azomethine [3]. When two equivalents of salicylaldehyde are combined with a diamine, a particular chelating Schiff base is produced. The so-called Salen ligands with four coordinating sites and two axial sites open to ancillary ligands. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in literature to describe the class of [O,N,N,O] tetradentate Schiff base ligands [3, 7]. Salen type Schiff base represents a versatile series of ligand. In attention to importance of these compounds many literatures have been published in this field [8]. They are facing a growing interest due to their various applications, e.g. as anticancer, antibacterial, antiviral, antifungal, and about their other biological properties [9].

Symmetric and asymmetric transition metal complexes of these bases have been developed and used as ligands/catalysts in many reactions such as epoxidation, asymmetric synthesis, asymmetric sulfoxidation, asymmetric silylcyanation and many other applications [10-12]. Schiff bases and the relevant transition metal complexes are still found to be of great interest in inorganic chemistry, although this subject has been studies extensively. Schiff bases play a central role as chelating ligands in main group and transition metal coordination chemistry [13,14].

Stability constants of metal ion complexes of various ligands and especially chelating ligands using different methods such as potentiometric, conductometric and spectrophotometric techniques have been determined. Stability constant of a complex ion is influenced by factors such as ligand type, metal ion type, counter-ions and solvent [15-22]. Spectrophotometric methods are, in general, highly sensitive, and as such are suitable for studying chemical equilibria in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and the determination of equilibrium constant is trivial. Several spectrophotometric methods have been developed to determine the equilibrium constants of chemical processes [23, 24].

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

2. Materials and methods

2.1. 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%), 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 (cobalt chloride, sodium hydroxide, and 37% hydrochloric acid) were ACS reagent grade and obtained from MERCK. The stock of 1.00x10-3 M solutions of salen in five solvents was prepared. The stock of 1.00x10-3 M solutions of Co(II) in deionized water and methanol were also prepared. The Milli-Q water was used in this study.

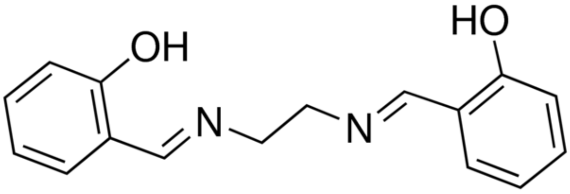


Fig 1. N,N′-Bis(salicylidene)ethylenediamine (salen)

2.2. Spectrophotometric Analysis

The UV-VIS absorption spectra were developed using the Agilent Cary 60 UV-Vis Spectrophotometer in the range from 200 to 500 nm. Spectra were recorded at 25°C. To study the effect of solvent on absorption spectrum of Co-salen complex, a series of diluted solutions (approximately 1.00×10^{-5} M) in each solvent were used.

2.3. Complexation Study

The absorption maxima of Co-salen complex in different solvents were investigated by titration of 1.00×10^{-5} M salen solution with 1×10^{-3} M Co(II) solution (20 µl additions) and recording the spectrum (from 200 – 500 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) [25] and mole ratio method [26].

2.4. Conductometric Analysis

Conductometric measurements were performed using a Jenway 4510 conductivity meter. A conductivity cell made of quartz was used. The cell constant at 25 C° was determined by conductivity calibrations of a 0.010 M solution of analytical-grade KCl (Merck) in deionized water. The standard procedure was as follow: 20.0 ml of metal ion solution (5.0×10^{-4} mol.L^{-1}) prepared in the tested solvent was putted in the titration cell and the conductance of solution was measured. Then a known amount of (5.0×10^{-3} mol.L^{-1}) salen solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. The salen ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

3. Results and discussion

3.1. Absorption Spectra of Salen in Different Solvents

The spectra of the saline in the non-aqueous solvents under investigation are shown in Fig 2. As shown, saline exhibits two absorption peaks, one at wavelength of 260 nm and the other at wavelength of 320 nm, which varies with each solvent. The second absorption peak shows the contribution of the n electrons on nitrogen atoms of the salen ligand (due to the conjugation of π electrons with the n electrons), which will be affected by the complexation between salen ligand Co(II) ions.

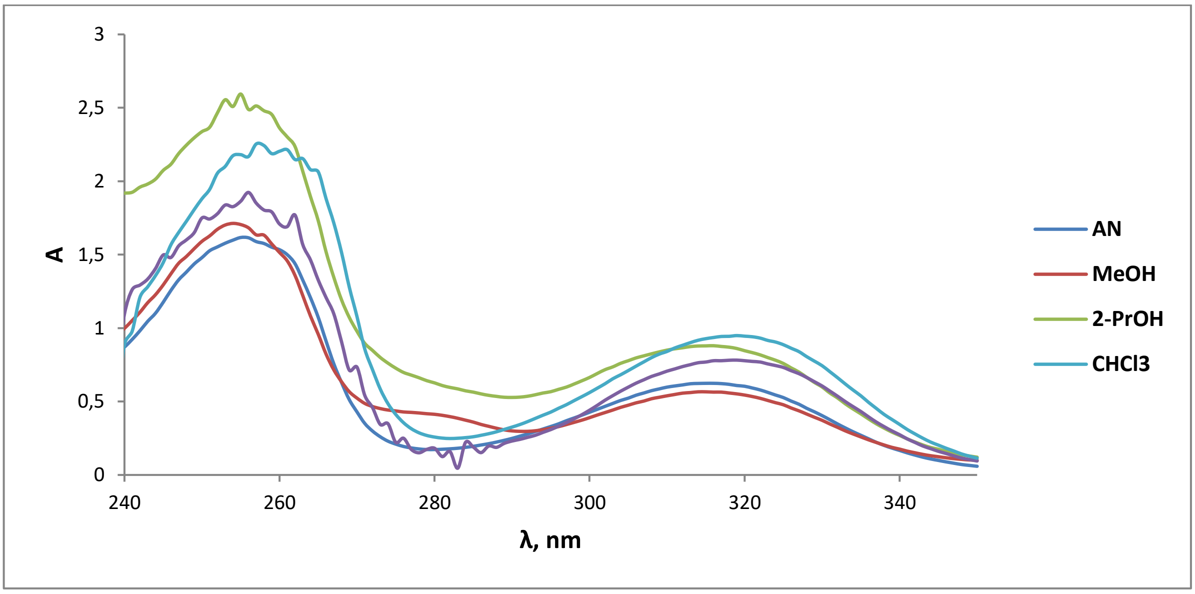
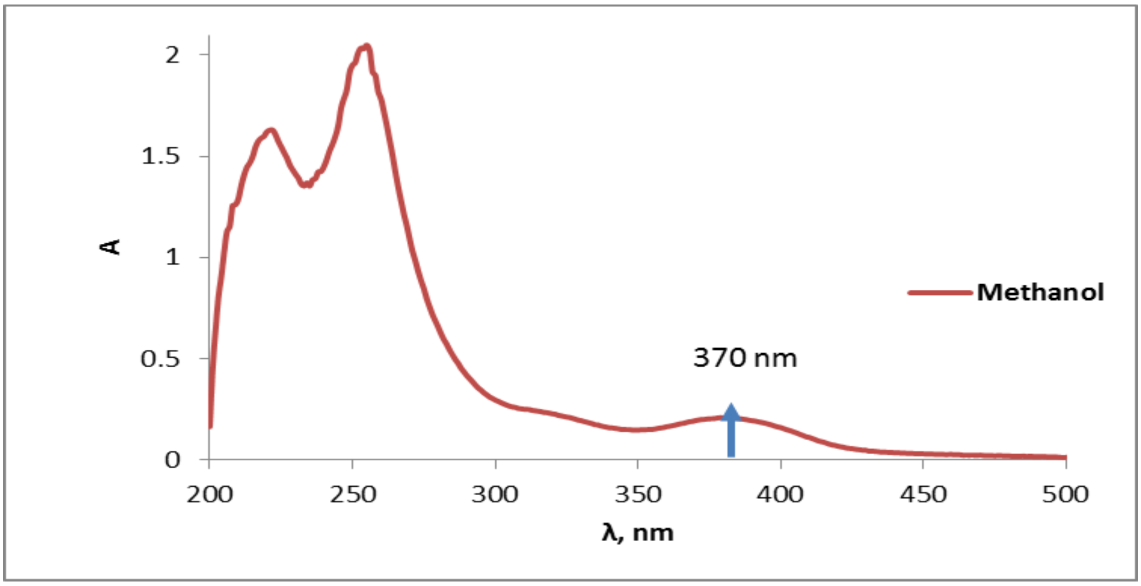
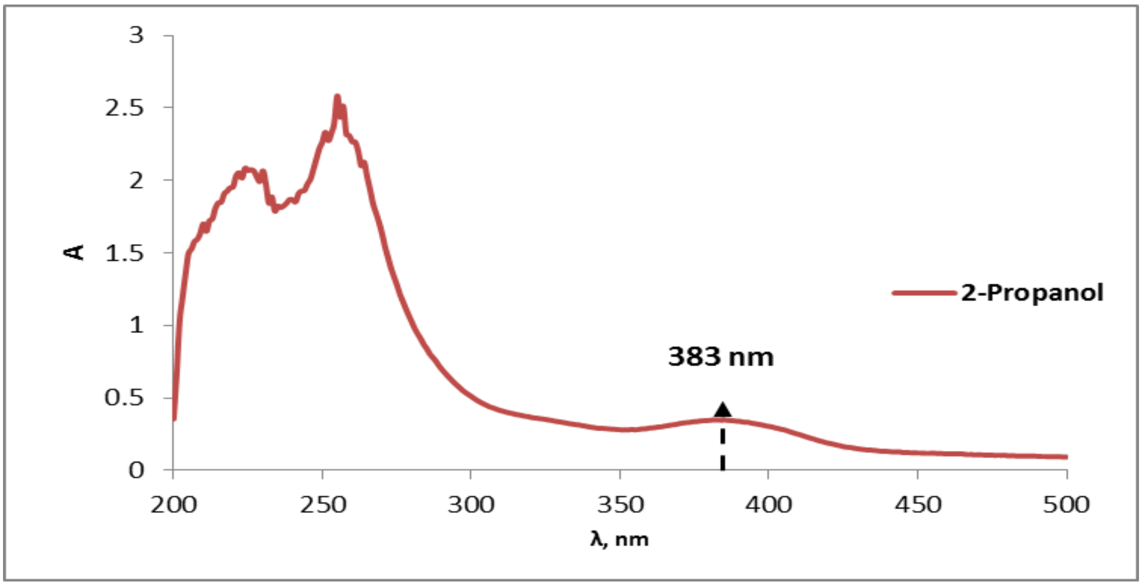


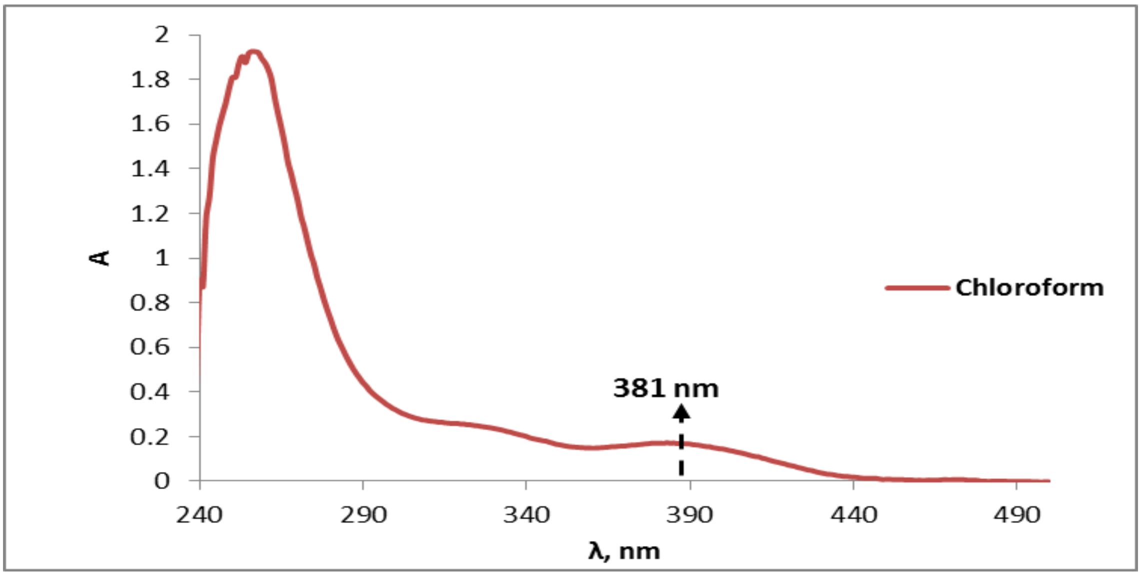
Fig 2. Absorption spectra of salen in different solvents

3.2. Complexation of salen with Co(II) in different solvents

The complexation of the saline with Co(II) ions resulted in a red shift of the second salen absorption peak (at 320) as shown in Figure 3. After complexation with cobalt ions, the second absorption peak was redshifted to the following wavelengths: 370, 380, 366 nm, 381, and 383 in methanol, acetonitrile, chloroform, and 2-propanol, respectively. The donation of the non-bonding electron on the nitrogen atoms of the saline to the Co(II) ions caused this displacement. The difference in energy between the ground states and excited states in salen became lesser after coordination with Co(II) ions, because the excited state energy decreased by more extent than the ground stat, and as a result a red shift of the absorption peak occurred after coordination


A
2
1.5
1
0.5
0
200
250
300
350
400
450
500
λ, nm
Methanol
370 nm


A
3
2.5
2
1.5
1
0.5
0
200
250
300
350
400
450
500
λ, nm
2-Propanol
383 nm


A
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
240
290
340
390
440
490
λ, nm
Chloroform
381 nm

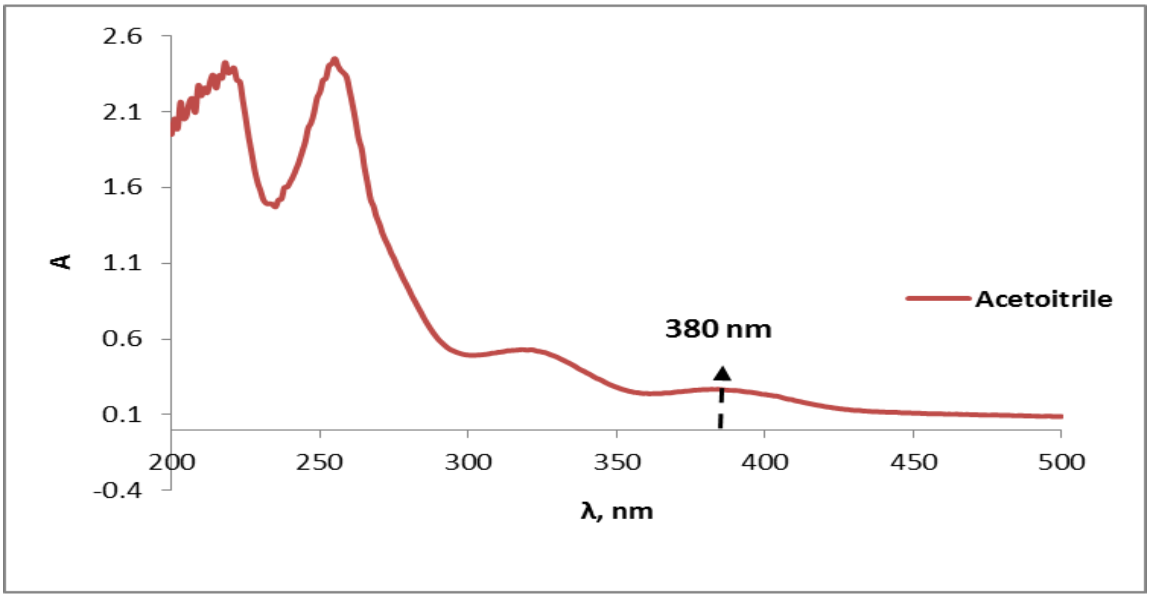


Fig 3. Spectra of free salen and Co-salen complex in different solvents

3.3. Time Effect

Time is one of the most important parameters that must be studied in the complex formation process, as it is likely that the complex could be dissociate in a short period of time after its formation. The Co(II) ions and salen solutions are mixed together at room temperature, and the absorbance of the resulting complex is measured at different time intervals. In this study, the absorption of the complex is recorded each 15 min as shown in Figure 4. The absorbance of the complexes increases in all solvents with time indicating that the complexes still formed with time till reach the equilibrium after about 60 min.

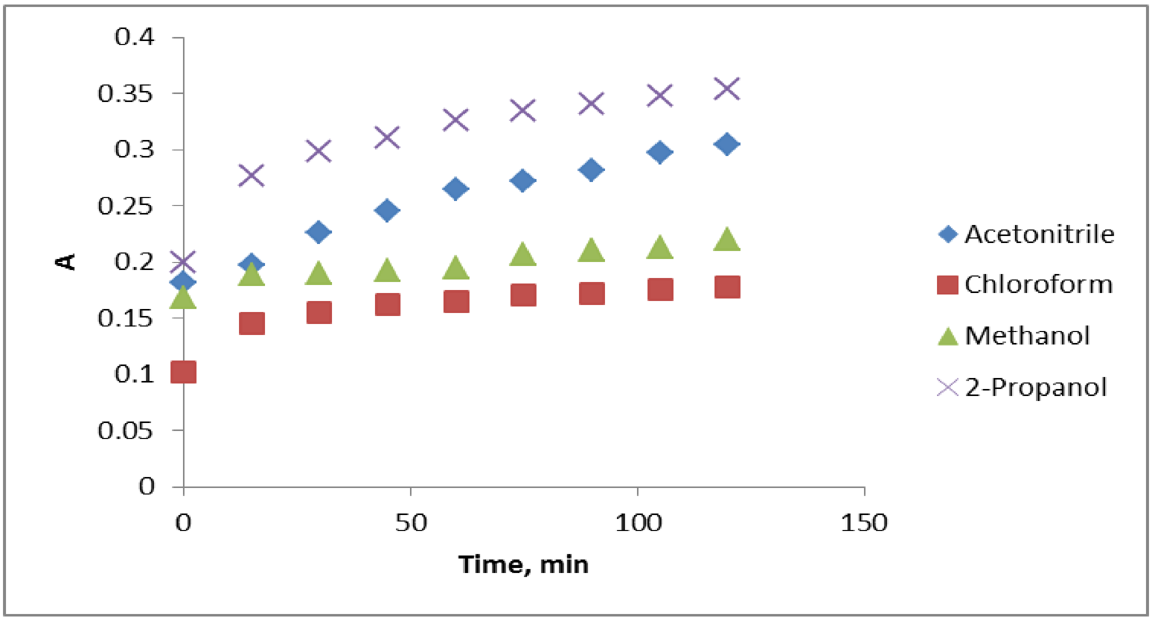


Fig 4. Effect of time on Co-salen complex in different solvents

3.4. The Stoichiometry of the Complexes and the Formation Constants (Kf) by Job's Method

The stoichiometry of the complexes formed in each solvent were evaluated by the method of continuous variation (Job's method). These absorbance values for 9 mixtures with different Co(II) : salen ratios were drawn against ligand mole fraction and from which the stoichiometry and formation constant of the complex in each solvent were determined. Job's plot for the complex formed in each solvent are shown in Figure 5. In the same way, the molar absorptivity ε of the complexes were also determined by calculating the concentrations of the complexes at each point and plotting the concentration against the absorbance (Figure 6). The complex stoichiometry, formation constant, and molar absorptivity values are given in Table 1. The molar absorptivity values indicate that the all transitions which occurred are of type π → π*.

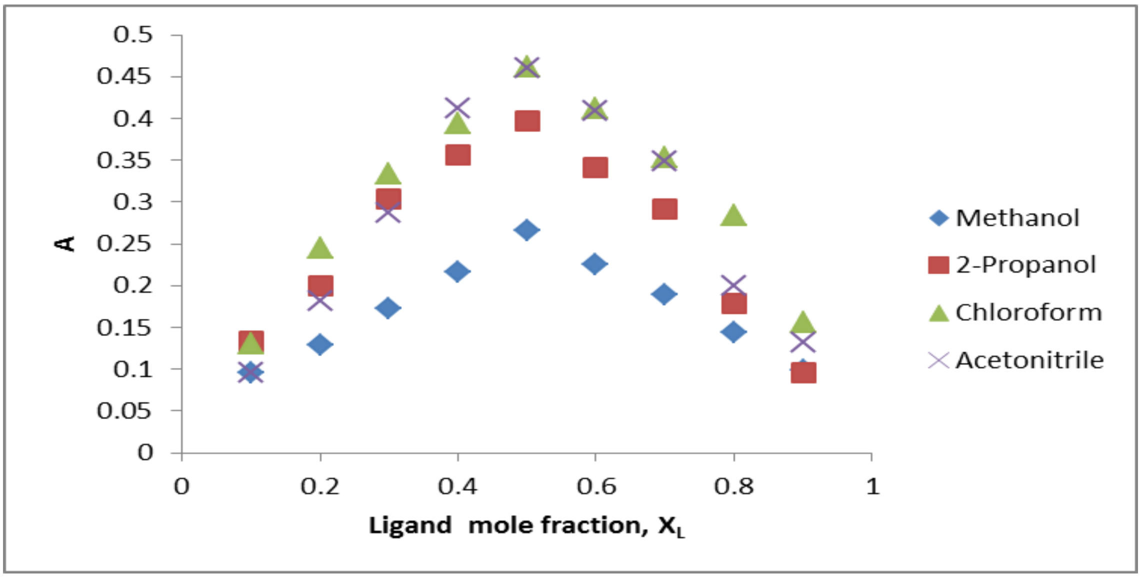


Fig 5. Job's plot of Co-salen complex in different solvents

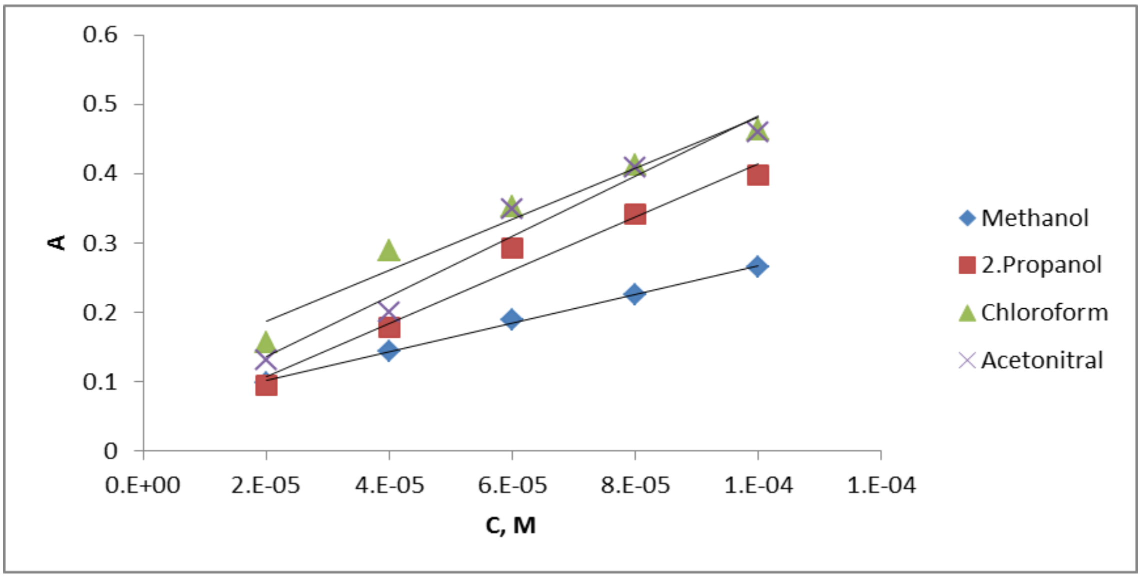


Fig 6. Calibration curve of Co-salen complex in different solvents by Job's method

Table 1. Co-salen complexes λ_{max}, stoichiometry, and formation constant values by Job's Method and Mole Ratio's Method methods

Solvent	λ_{max} (nm)	m:n	Job's Method			Mole Ratio's Method		
			$LogK_f$	ε ($L.mol^{-1}.cm^{-1}$)	R^2	$LogK_f$	ε ($L.mol^{-1}.cm^{-1}$)	R^2
MeOH	370	1:1	9.85	2074	0.997	9.61	2922	0.977
2-PrOH	383	1:1	9.88	3831	0.975	9.54	3147	0.999
AN	380	1:1	9.65	4326	0.963	10.02	4356	0.989
$CHCl_3$	381	1:1	10.35	4326	0.956	10.62	3994	0.996

The stoichiometry of all Co-salen complexes were 1:1 and the stability in each solvent had the following order: Chloroform > 2-propanol ~ Methanol ~ Acetonitrile. It is noted that the complex formed in chloroform is more stable and has a larger formation constant, this is because metal ions are less solvated by chloroform molecules than by the other solvents.

3.5. The Stoichiometry of the Complexes and the Formation Constants (K_f) by Mole Ratio Method

An ideal mole-ratio plots between Co(II) mole ratios and complex absorbance are displayed in Figure 7. Stoichiometry and formation constants for the complexes formed in each solvent were evaluated from the data in the curved portion of mole-ratio plots where the reaction is least complete.

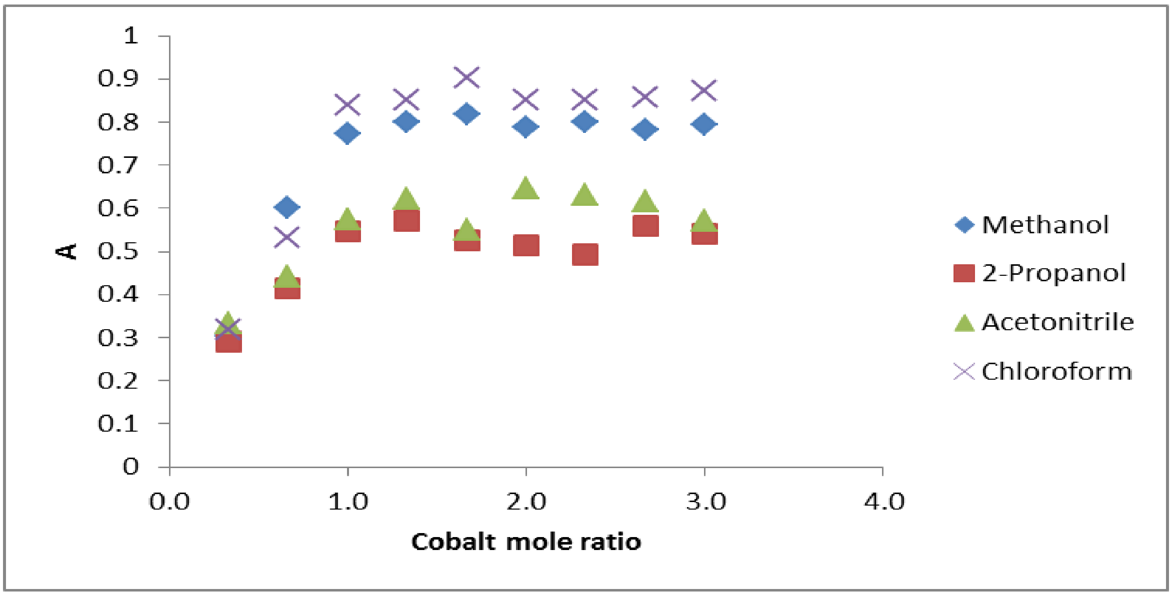


Fig 7. Mole Ratio's plot of Co-salen complex in different solvents

The molar absorptivity ε values were also determined using Mole Ratio's method by calculating the concentrations of the complexes at each point and plotting the concentration against the absorbance (Figure 8). The complex stoichiometry, formation constant, and molar absorptivity values are presented in Table 1. The stoichiometry of all Co-salen complexes were 1:1 and the stability in each solvent had the following order: Chloroform > Acetonitrile > 2-propanol ~ Methanol.

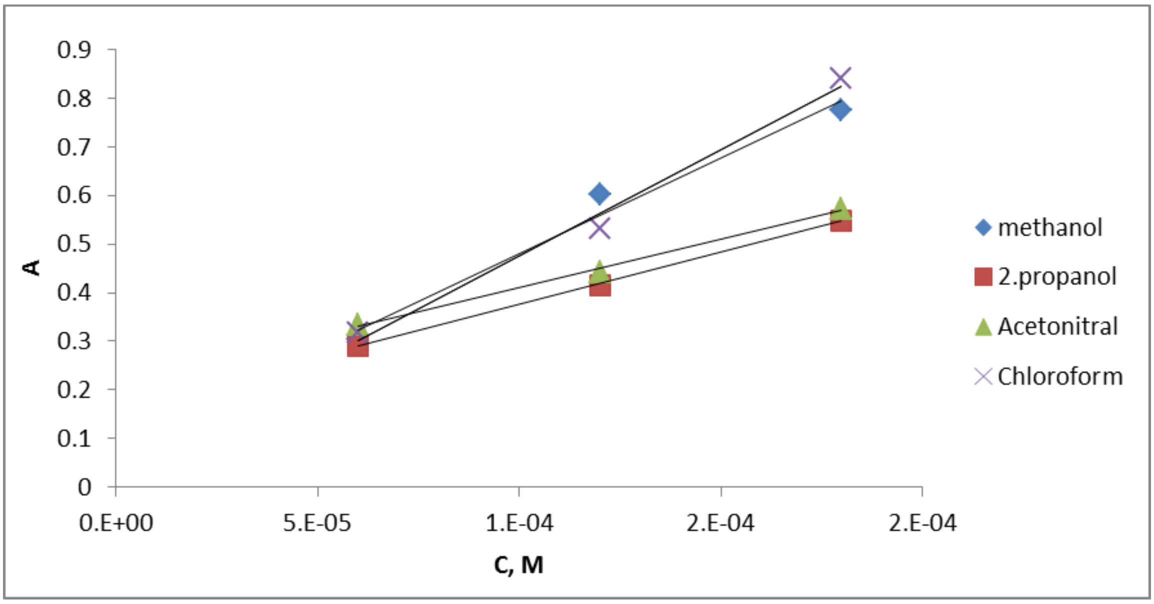


Fig 8. Calibration curve of Co-salen complex in different solvents by Mole Ratio's method

3.6. Conductometric Study

To gain an insight into the nature of Salen / cation complexation behavior, the changes of molar conductance (Λ_m) with ($[L]_t/[M]_t$) mole ratio for the complex formation of Salen with Co^{+2} cation in pure MeOH, PrOH, MeCN and $CHCl_3$ at 25°C using the conductometric method were investigated. The resultant molar conductance (Λ_m) versus Salen/Co^{+2} molar ratios ($[L]_t/[M]_t$) are plotted and shown in Figure 9. As it is obvious from the figure, addition of Salen to a solution of the Co^{+2} cation in all solvents shows an increase in molar conductivity with an increase in the ligand concentration. This could be due to a higher mobility of [Salen/Co^{+2}] complex compared with free solvated Co(II) cations. From Figure 9, it is clear that the molar conductance/molar ratio plots possess changes in the slope which can be recognized on a careful look at the conductance / molar ratio plot at the molar ratio of 1 indicating a formation of [Co(Salen)] complex in all solvents. The log K_f data of the Salen complex in pure MeOH, PrOH, MeCN and $CHCl_3$ at 25°C are listed in Table 2. It is documented that the donor ability and dielectric constant of the solvent play a vital role in complexation reactions [27,28]. Comparison of the data given in Table 2 indicates that the stability of the ML complexes decreases in the order $CHCl_3$ > MeCN > PrOH > MeOH. This can be understood by considering the relative solvating ability of the pure organic solvents. MeOH (DN = 20.0) with a relatively high donor ability relative to, PrOH (DN=18), MeCN (DN = 14.1) and $CHCl_3$ (DN =6.5), can solvate the Co^{+2} cation strongly and compete with the Salen ligand for this cation in the solution. In addition, the high dielectric constant of MeOH ($\mathcal{E}$ = 32.6), compared with PrOH (Ɛ =20.1), MeCN (Ɛ = 36) and $CHCl_3$ (Ɛ = 4.81) could also lead to a decrease in electrostatic interactions between the ligand and cobalt cations in solution. Although the dielectric constant of MeCN is greater than that of MeOH, the stability constant of the [Co(Salen)] complex in MeOH was lower than that in MeCN. This behavior may be attributed to the point that the donor ability of the solvent plays the most important role in complex formation in solution [29]. However, the stability order of Salen complexes which was obtained in this work is with good agreement with our previous reported work [5].

In order to understand the thermodynamics of the complexation reaction between the Co^{+2} ions and Salen ligand, the enthalpy and entropy contributions to this reaction were evaluated. The values of the enthalpy ΔH and the entropy ΔS for the complexation reaction in methanol were evaluated from the temperature dependence of the formation constants by applying a linear least-squares analysis, according to the van't Hoff equation [30]. The values of ΔH and ΔS are obtained from the slope of van't Hoff plots and the intercepts, respectively, while ΔG is determined from the following equation:

$$\Delta G = -RT \ln K_f \qquad (1)$$ [30]

$$\Delta G = \Delta H - T\,\Delta S \qquad (5)$$ [30]

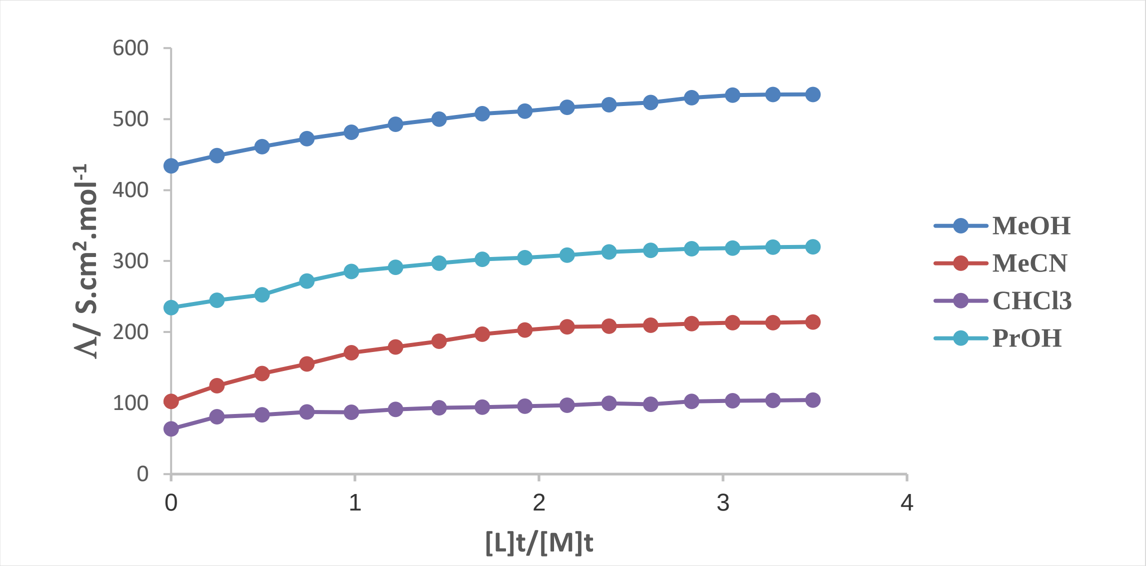


Fig 9. Molar conductance vs mole ratio plots for (Salen/Co^{+2}) complexes in MeOH, MeCN, PrOH and $CHCl_3$

Figure 10 shows the changes of molar conductivity (Λ_m) versus the ligand to the cation molar ratio for the complexation of Salen and Co^{+2} in methanol at different temperatures. The stability constants, standard Gibbs energy, enthalpies and entropies of [Co(Salen)] complex in MeOH solvent at different temperatures are listed in Table 3. The stability constant values increase with increasing temperature which means that the complexation reaction between Salen and Co^{+2} is an endothermic process. The negative value of ΔG shows the ability of the Salen ligand to form stable complex with cobalt(II) and the process trend to proceed spontaneously. However, the obtained positive value of ΔH (Table 3) means that enthalpy is not the driving force for the formation of the complex. The positive value of ΔS (Table 3) indicate that entropy is responsible for the complexing process.

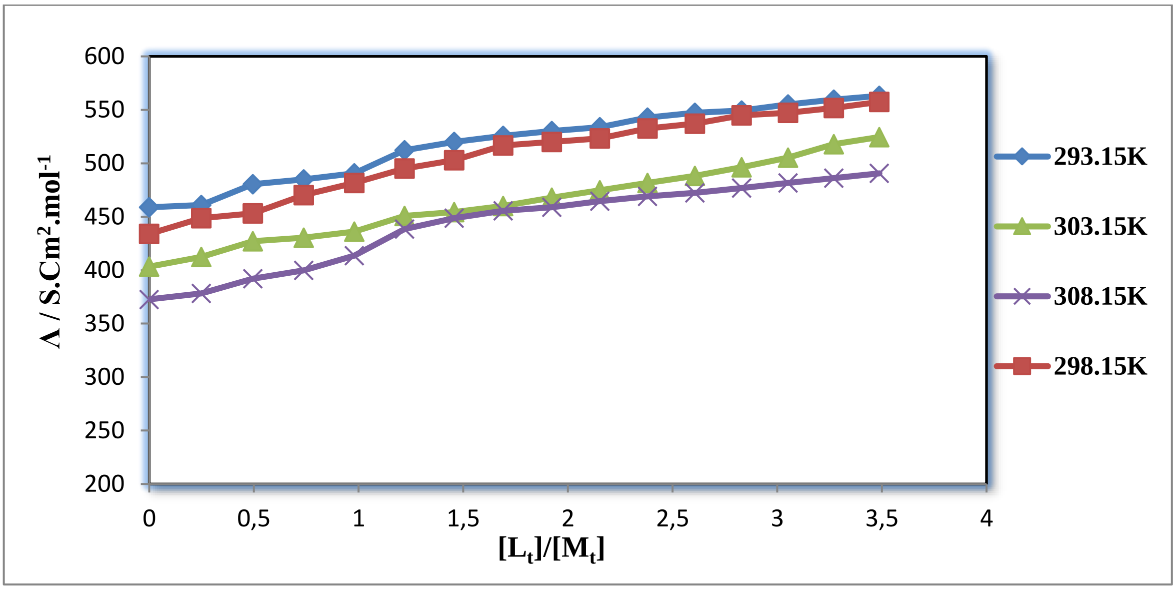


Fig 10. Molar conductance-mole ratio plots for [Co(Salen)] complex in MeOH at different temperatures

Table 2. log K_f values of the Salen complex with cobalt(II) in various solutions at 25 ˚C

Solvent medium	$CHCl_3$	MeCN	PrOH	MeOH
log K_f	4.53	4.36	4.12	3.46

Table 3. Stability constants and thermodynamic parameters for [Co(Salen)] complex in MeOH at different temperature

T (K)	Log K_f	ΔG ($KJmol^{-1}$)	ΔH ($KJmol^{-1}$)	ΔS ($KJmol^{-1}$)
293.15	3.34	-19.11	21.37	137.34
298.15	3.46			
303.15	3.49			
308.15	3.53			

Conclusion

In this study, the spectroscopic investigation of the complex formation process between saline ions (Bis (salicylidene) ethylenediamine) and Co (II) in a number of non-aqueous solvents showed that all the complexes formed were with a mole ratio of 1: 1. The formation constants were also determined using two spectroscopic methods in each solvent. The formation constant of Co (II) -salen in chloroform was the highest while in methanol was the lowest. This is because Co (II) ions were less solvated in chloroform and thus can be easily complexed than in methanol. The conductometric measurements indicated the complexes formed in all solvents were with a ratio of 1:1, and also the complex formed in chloroform was the most stable complex. The thermodynamic study of the complex in a methanol solvent showed that the complex formation process was an endothermic and spontaneous process and the entropy was responsible for the formation of the complex.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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