

## Complexation and Thermodynamic Studies of a New Schiff base Ligand with Some Metallic ions in Nonaqueous Solvents by Conductometric Method

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### Abstract

The complexation reactions between N-N'-Bis(5-bromo-2-hydroxybenzylidene)-2,2-dimethylpropane-1,3-diamine Schiff base ligand and Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup> ions were studied conductometrically in acetonitrile, dimethylformamide, ethanol, and methanol solvents at 5, 10, 15, and 25°C. The formation constants of the resulting ML and M<sub>2</sub>L complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. The selectivity of the Schiff base ligand to the cations is depended the nature of the solvent. At 25°C in acetonitrile solvent, the stability of the resulting complexes varied in the order Hg<sup>2+</sup> > Ag<sup>+</sup> > Cd<sup>2+</sup> > Cu<sup>2+</sup> > Co<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup>. It was found that the stability of the resulting complexes decreased with increasing the solvation ability of the solvent. The values of the thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ ) for complexation reactions were obtained from the temperature dependence of the stability constants values (log  $K_f$ ) using the Van't Hoff plots. In most cases, the complexes were found to be an enthalpy and entropy stabilized.

### Keywords

Complexation; Conductometric; Formation Constants; Schiff Bases; Thermodynamic Parameters.

### 1. INTRODUCTION

The coordination chemistry of nitrogen-oxygen donor ligands is an interesting area of research with lots of potential information to focus on. A great deal of attention has been focused on the complexes formed between transition metal ions and Schiff bases because of the presence of both nitrogen and oxygen donor atoms in the structure of these ligands [1, 2]. Metal ions coordinate to a Schiff base ligand through the imine nitrogen (HC=N-) and another donor atom group, usually oxygen, which is important in illustrating their reaction mechanism [3]. The study of Schiff base complexes is of great importance because of the capability offered by these complexes in the fields of catalysis [4, 5], drug research [6-7], photochromic properties [8, 9], organic synthesis [10-11] and analytical applications [12-13].

The study of the complexation reaction of Schiff bases with metal ions in non-aqueous matrices to design the analytical systems, not only results effective information about complexation, but also lead to a better understanding of the selectivity of these ligands toward different metal cations [14]. It is important to investigate the dependence of the stoichiometry, stability constants, and thermodynamic parameters of the Schiff base ligand-cation complexes on the nature of solvents to see how the thermodynamics of

complexation are affected by the kind of solvent [15]. The Schiff base-M<sup>n+</sup> complexes in solution could result after a series of reactions including: (i) partial or complete desolvation of the cation, (ii) partial or complete desolvation of the ligand, (iii) conformational change of the Schiff base ligand, (iv) formation of the ligand-cation complex and (v) solvation of the resulting complex. As is evident, the solvent molecules are directly involved in three of the five possible equilibria [16]. Thus, it is expected that the solvent properties such as hard and soft basicity scales [17], Coordination power [18], Dielectric constant of the solvent [19], and Guttmann donocity scale [20] will affect the process of complexation considerably. In recent years some physicochemical techniques such as NMR spectrometry [14, 21], calorimetry [22, 23], voltammetry [24, 25], spectrophotometry [3, 26], conductometry [15, 27], and potentiometry [23, 28] have been used to study the complex formation between Schiff bases and transition metal cations in solutions. Among these various methods, the conductometric technique is a sensitive, accurate, and inexpensive method with a simple experimental arrangement for such investigations.

In this study, the influence of solvent properties on the thermodynamic parameters of complex formation between N-N'-Bis(5-bromo-2-

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hydroxybenzylidene)-2,2-dimethylpropane-1,3-diamine Schiff base ligand (**L**) [29] (Fig.1) with some transition metallic ions in Acetonitrile (AN), Dimethylformamide (DMF), Ethanol (EtOH) and Methanol (MeOH) based on the conductometric method at different temperatures was investigated.

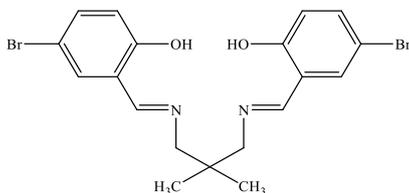


Fig. 1. Chemical structure of Schiff base ligand (**L**)

## 2. EXPERIMENTAL

### 2.1. Reagents and apparatus

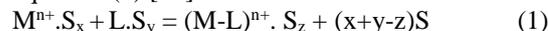
Analytical reagent grade nitrate salts of silver, chromium, cobalt, nickel, zinc, cadmium, mercury, lead, and spectroscopic AN, DMF, EtOH, MeOH solvents (obtained from Merck), were used as received without any further purification. Solutions of all ions at  $5 \times 10^{-5}$  M concentrations and Schiff base ligand at  $5 \times 10^{-3}$  M concentration were prepared by dissolving the accurately weighed amount of reagents in the proper volume of solvents. The conductance measurements were carried out using a Metrohm (model 712) conductometer with a platinum electrode in a dip-type conductivity cell. During the experiments, the cell was thermostated at the desired temperature within  $\pm 0.01^\circ\text{C}$  with a Julabo ED circulator.

### 2.2. Conductometric procedure

In order to evaluate the influence of adding Schiff base ligand on the molar conductance of metal ions in different solvents, the molar conductance at a constant salt concentration ( $5 \times 10^{-5}$  M) was monitored while increasing the Schiff base ligand concentration at various temperatures. In a typical experiment 10 mL of the desiring metal nitrate solution ( $5 \times 10^{-5}$  M) in acetonitrile was placed in the two-wall conductometer glass cell equipped with a magnetic stirrer, thermostated at the desired temperature and the conductance of the solution was measured and to keep the ionic strength constant during the experiment the solution in the titration vessel was mixed using a magnetic stirrer. Then a known amount of the concentrated solution of Schiff base ligand in acetonitrile ( $5 \times 10^{-3}$  M) was added in a stepwise manner using a 10  $\mu\text{L}$  Hamilton syringe. The conductance of the solution was measured after each addition. The addition of the ligand was continued until the desired ligand to cation mole ratio was achieved. Then this procedure was repeated in the other solvents.

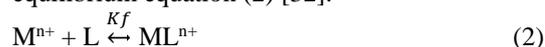
### 2.3. Complex Formation Constant ( $K_f$ )

The complex reaction between the Schiff base ligand and a target cation in a solution is an equilibrium process and can be considered as equation (1) [30].



Where S is the solvent molecule, and x, y and z are the solvation numbers of the ions, the ligand, and the resulting complex, respectively.

The complex formation constant, the Gibbs free energy of the complexation process, and its enthalpy and entropy in the solutions can be affected by the solvation of the target cation, ligand, and resulting complex [31]. The complex stability of a transition metal ions with a Schiff base ligand depends on a range of factors including the number and type of donor atoms and the donor ability of the solvent expressed as the Gutmann acceptor and donor number, dielectric constant of the solvent, shape, and size of the solvent molecules and the nature of metal cation [15]. The binding of transition metal cation with the Schiff base **L** can be represented by the equilibrium equation (2) [32].



And the corresponding equilibrium constant,  $K_f$ , is given by equation (3).

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \frac{f(M^{n+})f(L)}{f(ML^{n+})} \quad (3)$$

where  $[ML^{n+}]$ ,  $[M^{n+}]$ ,  $[L]$  and  $f$  are the equilibrium molar concentrations of the complex, free cation, free ligand, and the activity coefficients of the species indicated, respectively. In highly dilute conditions, the activity coefficient of uncharged ligand,  $f(L)$ , can be reasonably assumed as unity [33, 34]. Using the Debye Hückel limiting law leads to the conclusion that  $f(M^{n+}) = f(ML^{n+})$ , so the activity coefficients in equation (3) can be omitted. Thus, the complex formation constant in terms of the molar conductance can be expressed as the equation (4) [35-36].

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_{M^{n+}} - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (4)$$

Where  $[L]$  is represented as the equation (5).

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (5)$$

Here,  $\Lambda_M$ , is the molar conductance of the metal nitrate before the addition of the ligand,  $\Lambda_{obs}$  is the molar conductance of solution during the titration,  $\Lambda_{ML}$  is the molar conductance of the complex,  $C_L$  and  $C_M$  are the concentrations of the ligand added, and the metal nitrate, respectively. The mass balance equations in solution are given as equation (6) and (7) for metallic ion and the ligand concentration, respectively.

$$C_M = [M^{n+}] + [ML^{n+}] \quad (6)$$

$$C_L = [L] + [ML^{n+}] \quad (7)$$

where  $C_M$  and  $C_L$  are the initial analytical concentration of  $M^{2+}$  and the Schiff base ligand, respectively. The mass balance equations for the

1:1 model can be solved to obtain an equation for the ligand concentration, [L], as equation (8), and for mixed (M<sub>2</sub>L and ML) complexes as equation (9) [27].

$$K_f[L]^2 + (1 + K_f C_M - K_f C_L)[L] - C_L = 0 \quad (8)$$

$$K_{f1}K_{f2}[L]^3 + K_{f1}(1 + K_{f2}(2C_M - C_L))[L]^2 + (1 + K_{f1}(C_M - C_L))[L] - C_L = 0 \quad (9)$$

The formation constant ( $K_f$ ) and the molar conductance of the resulting 1:1 and 2:1 (metal ion to ligand) complexes between the Schiff base ligand and different cations were calculated at different temperatures by fitting the observed conductance,  $\Lambda_{obs}$ , at various metal ion/ligand mole ratios to the (8) and (9) equations, which express the  $\Lambda_{obs}$  as a function of the free and complexed ligand. The formation constant evaluated from a non-linear least-squares program KINFIT [37].

#### 2.4. KINFIT program

Curve fitting, statistical, and numerical analysis are often a major and inevitable part of chemical experimentation. In this context, many packages were written for mainframe computers and extensively used for many years. Of these, the most popular for the evaluation of formation constants of metal complexes are LETAGROUP [38-39], SQUAD [40], DALSFEX [41], and KINFIT [37]. All are based on the minimization of the sum of squared of residual (SSR), but they differ in the iterative procedure they use to approach a minimum of SSR. In this paper, the nonlinear least squares curve-fitting program KINFIT was used for evaluation of the formation constants from the molar conductance versus  $C_M/C_L$  mole ratio data [42]. KINFIT is a Data processing program for minimizing the sum of squared deviations between the measured and estimated data using a non-linear fitting algorithm based on the so-called Simplex method [37, 43].

#### 2.5. Thermodynamic parameters

To gain a better understanding of the thermodynamics of the complexation reaction between L and metallic ions in the solvents, it is useful to determine the contribution of enthalpy and entropy of the reaction. The normal stability constant ( $K_f$ ) of the complex is related to the net changes of standard free energy,  $\Delta G^\circ$ , standard enthalpy,  $\Delta H^\circ$ , and standard entropy,  $\Delta S^\circ$ , of complexation. By calculating these functions, the effect of some important factors governing complex formation can be understood, such as solvation effects, the character of the coordinating bond, and the changes in the structure that often occurs during complex formation.

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the complexation reactions in different solvent solutions were determined from the temperature dependence of the formation constants of the resulting complexes by applying a linear least squares analysis according to the Van't Hoff formula as equation (10).

$$\ln K_f = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

The normal stability constant ( $K_f$ ) of the complex is related to the net changes of standard free energy,  $\Delta G^\circ$ , that the negative sign of the  $\Delta G^\circ$  shows that the ligand is capable of forming stable complexes and that the process will proceed spontaneously [29]. The value of  $\Delta G^\circ$  was calculated from the equations (11) and (12), where R and T are known as the universal gas constant and absolute temperature, respectively.

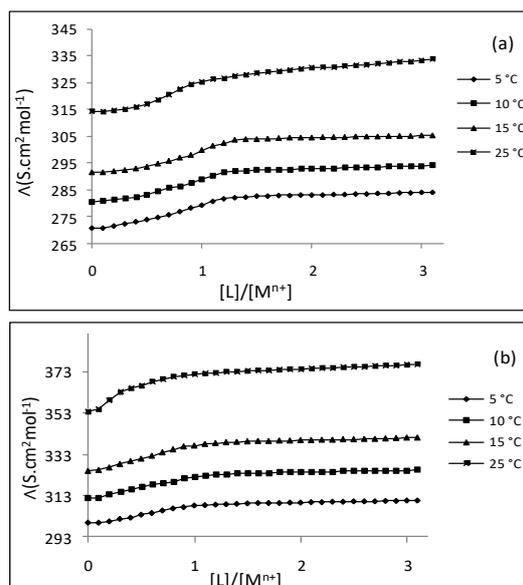
$$\Delta G^\circ = -RT \ln K_f \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

### 3. RESULT AND DISCUSSION

#### 3.1. Stoichiometry of the complex

The changes of molar conductance ( $\Lambda_m$ ) of the solution at a constant metallic salt concentration ( $5 \times 10^{-5}$  M) were monitored, while the concentration of ligand at various temperatures (5, 10, 15, and 25 °C) was increasing. In this research, the molar conductance ( $\Lambda_m$ ) versus ( $[L]/[M]_t$ ) mole ratio plots for the complex formation of the ligand with Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup> cations were studied in DMF, AN, EtOH and MeOH at different temperatures. Where,  $[L]_t$  is the total concentration of the ligand and  $[M]_t$  is the total concentration of the metal cations. Some examples of molar conductivity (L) versus  $[L]/[M]_t$  plots at different temperatures are shown in Figs. 2a and 2b. With the other systems, similar behavior was observed (data not shown). As expected, the corresponding molar conductance increased with temperature, due to the decreased viscosity of the solvent and consequently, the enhanced mobility of the charged species present.



**Fig. 2.** Molar conductance ( $S \text{ cm}^2 \text{ mol}^{-1}$ ) vs.  $[L]/[M^{n+}]$  plots in AN at various temperatures. The  $M^{n+}$  cations are (a) Hg<sup>2+</sup>, (b) Cu<sup>2+</sup>.

Molar conductance values as a function of  $([L]/[M])_t$  for  $L-M^{n+}$  complexes in acetonitrile at 25 °C are shown in Fig. 3. Since the ligand concentration was low, the change in viscosity was deemed too small to warrant making corrections. As can be seen, by increasing the ligand concentration, molar conductance of  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Ag^+$  ion solutions decreased. While the conductance behavior of  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  show a gradual increase in molar conductivity with an increase in the ligand concentration ion solutions is not similar to them, their molar conductivity decreases. Which can be explained based on the solvation sphere and considering the *charge/radius ratio* of the ions.

Based on the ionic radius of the transition elements [44],  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  ions have lower *charge/radius ratio*. Such ions have less solvation after dissolving of their nitrate salts, which causes stronger interactions with nitrate ions and leads to lower molar conductance of the solution before adding the Schiff base. Then, the addition of the ligand forms a complex that decreases the interaction of  $NO_3^-$  anion with these cations, and hence increases the conductance of the solution.

But  $Co^{2+}$ ,  $Ni^{2+}$  ions have higher *charge/radius ratio causing more solvation their nitrate salts*. The ion pairs of such ions are expected to dissociate into ions and the counter ion ( $NO_3^-$ ) have less interaction with cations, which leads to higher molar conductance of the solution before adding the Schiff base. By increasing the ligand to the solution, these molecules replace the solvent molecules around the metal ion and form a complex that has less conductivity than the initial solvated ion. In this case, the molar conductance of the solution gradually decreases. In these conditions, even the nitrate ions become closer to the complex and help to reduce the conductance of the solution. The silver ion has a lower *charge/radius ratio* and less solvation. Its interaction with nitrate ion is weak, which leads to higher molar conductance of the solution before adding the Schiff base. When complexes with Schiff base are formed, they become bulkier, causing a decrease in its mobility and also in the molar conductance of the solution.

The slope of curves in Fig 3, shows change sharply at the point where the  $[L]/[M^{n+}]$  is about 0.5 and 1. Further addition of the ligand causes no or very slight changes in the molar conductance. This suggests the formation of ML complex for all the six cations but two complexes with the formulas  $M_2L$  and ML for  $Hg^{2+}$ .

The analysis of the X-ray crystallography data of the Schiff base L proved that the ligand has a flexible structure[29]. This flexible structure provides the possibility of forming a  $M_2L$

complex for mercury ion. The proposed molecular structures of the  $M_2L$  and ML complexes for mercury(II) ion are shown in Fig. 4.

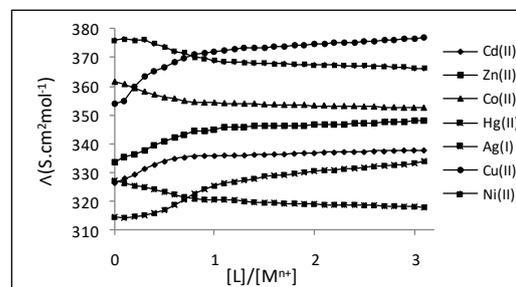


Fig. 3 Mole ratio plots of the metal ions with ligand L in AN solution at 25 °C

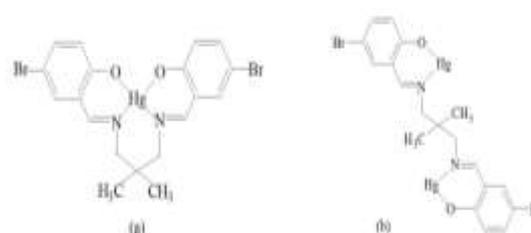
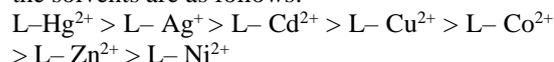


Fig. 4 The proposed molecular structures of the complexes for mercury(II) ion: a)ML, and b)  $M_2L$

### 3.2. Stability constant of the complexes

The complex formation constant ( $K_f$ ) for all formed complexes in each solvent at various temperatures was calculated from changes of the molar conductance as a function of  $[L]/[M^{n+}]$  molar ratio using a non-linear least squares program KINFIT computer program. The results are shown in table 1. By comparison of the formation constants, it is concluded that the  $K_f$  value of complexes with metal cations varies in the solvents are as follows:



The results shown in Table 1 are in good agreement with the theoretical calculations based on the donor properties of the solvent [45]. Generally, in solvents with a high donor ability and dielectric constant, the stability constant of the complex should decrease owing to the competition between the ligand and the solvent molecules for the metal ion [46]. The stability constant of the  $L-M^{n+}$  complex among various solvents decreases in the order  $AN(DN=14.1) > MeOH(DN=19) > DMF(DN=26.6) > EtOH(DN=30.4)$  [47]. This behavior reflects the much stronger cation solvation by EtOH, compared with the other solvents, with which the Schiff base has to compete. EtOH (Donor Number = 30.4 kcal mol<sup>-1</sup>) with a high donor ability can solvate the  $M^{n+}$  ions strongly and, therefore, compete with the ligand for the metal

ions. Therefore, in this solvent, the formation of the  $L-M^{n+}$  complex is weakened. In strong solvating solvents, such as EtOH, the metal ion is more strongly solvated and the complex formation is poor, whereas in solvents with medium donicites, such as AN and MeOH, a more stable complex is formed. It is interesting that although DMF and AN have comparable dielectric constants, the formation constant of the complex in AN, a poor donor solvent, is much higher than that in DMF, which has a larger donor number. This indicates that the dielectric constant of the solvent is not a dominant factor in this complexation reaction. It is noteworthy that, for each cation, the curvature of the corresponding mole ratio plot decreased with increasing temperature, indicating the formation of weaker complexes at elevated temperatures [48-49]. These are indicative of the decreased viscosity of solvents and the diminished stability of the resulting complexes at higher temperatures.

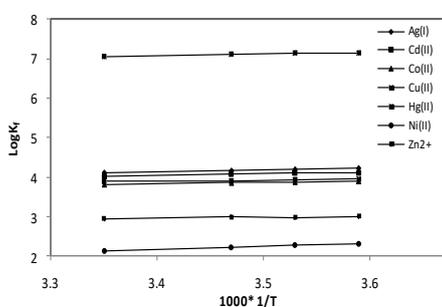
The enthalpies and entropies of complexation were determined from the slopes and intercepts of

the plots, according to the Van't Hoff equation, respectively. For example, the Van't Hoff plots of  $\log K_f$  vs.  $1/T$  for  $L-M^{n+}$  complexes in AN were shown in Fig. 5. The calculated thermodynamic parameters for complex formation are given in Table 1. The results show that the enthalpy and entropy values in most complexes are negative and positive, respectively. The values of standard entropy and standard enthalpy for the formation of complex in solution depended on different parameters such as changes in the flexibility of the ligand during the complexation process, solvation - desolvation of the species involved in the complexation reaction, and also with the extent of cation-solvent, ligand-solvent, complex-solvent and solvent-solvent interactions [50]. The increase in the degree of freedom caused by desolvation of cation might result in some positive entropic gain, as well as releasing the solvent molecules that involve in the interaction with the ligand in the complexation process [51].

**Table 1** Formation constant values and thermodynamic parameters for  $M^{n+}$ -L complexes at different temperatures

Solvent	Metal ion	Log Kf $\pm$ SD <sup>a</sup> at various temperatures				Thermodynamic parameters		
		5°C	10°C	15°C	25°C	$\Delta H$ (kJ. mol <sup>-1</sup> )	$\Delta S$ (J. mol <sup>-1</sup> . K <sup>-1</sup> )	$\Delta G$ (kJ. mol <sup>-1</sup> )
Acetonitrile	Ag <sup>+</sup>	4.23 $\pm$ 0.02	4.20 $\pm$ 0.01	4.17 $\pm$ 0.02	4.12 $\pm$ 0.01	-8.73	49.57	-22.76
	Cd <sup>2+</sup>	4.10 $\pm$ 0.01	4.11 $\pm$ 0.01	4.09 $\pm$ 0.01	4.02 $\pm$ 0.02	-6.84	54.26	-22.19
	Co <sup>2+</sup>	3.90 $\pm$ 0.02	3.88 $\pm$ 0.01	3.86 $\pm$ 0.02	3.82 $\pm$ 0.02	-6.36	51.82	-21.02
	Cu <sup>2+</sup>	3.95 $\pm$ 0.02	3.93 $\pm$ 0.01	3.91 $\pm$ 0.01	3.89 $\pm$ 0.01	-4.74	58.51	-21.30
	Hg <sup>2+</sup>	7.14 $\pm$ 0.01	7.15 $\pm$ 0.02	7.12 $\pm$ 0.02	7.06 $\pm$ 0.02	-6.94	112.05	-38.65
	Ni <sup>2+</sup>	2.31 $\pm$ 0.02	2.29 $\pm$ 0.01	2.22 $\pm$ 0.01	2.14 $\pm$ 0.02	-14.15	-6.53	-12.31
	Zn <sup>2+</sup>	3.01 $\pm$ 0.02	2.98 $\pm$ 0.01	2.99 $\pm$ 0.02	2.94 $\pm$ 0.02	-5.07	39.94	-16.21
Methanol	Ag <sup>+</sup>	2.96 $\pm$ 0.01	3.05 $\pm$ 0.02	3.23 $\pm$ 0.01	3.29 $\pm$ 0.02	-10.25	18.32	-19.54
	Cd <sup>2+</sup>	3.07 $\pm$ 0.02	3.02 $\pm$ 0.01	2.99 $\pm$ 0.02	2.93 $\pm$ 0.01	-10.83	19.68	-16.40
	Co <sup>2+</sup>	3.56 $\pm$ 0.02	3.54 $\pm$ 0.02	3.51 $\pm$ 0.02	3.45 $\pm$ 0.01	-8.89	36.28	-19.16
	Cu <sup>2+</sup>	3.62 $\pm$ 0.02	3.58 $\pm$ 0.01	3.59 $\pm$ 0.02	3.53 $\pm$ 0.02	-6.53	45.75	-19.48
	Hg <sup>2+</sup>	3.94 $\pm$ 0.02	3.95 $\pm$ 0.02	3.81 $\pm$ 0.02	3.78 $\pm$ 0.02	-14.57	23.16	-21.15
	Ni <sup>2+</sup>	2.77 $\pm$ 0.01	2.74 $\pm$ 0.02	2.70 $\pm$ 0.02	2.65 $\pm$ 0.02	-9.64	18.33	-14.83
	Zn <sup>2+</sup>	2.88 $\pm$ 0.02	2.69 $\pm$ 0.02	2.63 $\pm$ 0.01	2.54 $\pm$ 0.02	-25.08	-36.12	-14.86
DMF	Ag <sup>+</sup>	1.99 $\pm$ 0.01	1.97 $\pm$ 0.02	1.95 $\pm$ 0.02	1.92 $\pm$ 0.01	-5.55	18.11	-10.68
	Cd <sup>2+</sup>	2.38 $\pm$ 0.02	2.31 $\pm$ 0.01	2.25 $\pm$ 0.02	2.23 $\pm$ 0.01	-11.64	3.28	-12.57
	Co <sup>2+</sup>	2.59 $\pm$ 0.02	2.55 $\pm$ 0.02	2.37 $\pm$ 0.01	2.34 $\pm$ 0.02	-12.01	6.33	-13.80
	Cu <sup>2+</sup>	3.27 $\pm$ 0.02	3.22 $\pm$ 0.01	3.20 $\pm$ 0.01	3.14 $\pm$ 0.02	-9.92	26.79	-17.50
	Hg <sup>2+</sup>	3.09 $\pm$ 0.02	3.04 $\pm$ 0.02	2.99 $\pm$ 0.01	2.96 $\pm$ 0.02	-10.24	22.10	-16.49
	Ni <sup>2+</sup>	2.24 $\pm$ 0.02	2.19 $\pm$ 0.01	2.15 $\pm$ 0.02	2.14 $\pm$ 0.02	-7.71	14.85	-11.91
	Zn <sup>2+</sup>	2.84 $\pm$ 0.02	2.82 $\pm$ 0.02	2.75 $\pm$ 0.02	2.71 $\pm$ 0.02	-10.93	15.10	-15.20
Ethanol	Ag <sup>+</sup>	2.26 $\pm$ 0.02	2.22 $\pm$ 0.02	2.18 $\pm$ 0.02	2.11 $\pm$ 0.01	-11.91	0.42	-12.03
	Cd <sup>2+</sup>	2.32 $\pm$ 0.01	2.29 $\pm$ 0.02	2.25 $\pm$ 0.02	2.21 $\pm$ 0.01	-8.83	12.59	-12.40
	Co <sup>2+</sup>	1.49 $\pm$ 0.02	1.45 $\pm$ 0.01	1.44 $\pm$ 0.01	1.40 $\pm$ 0.02	-6.74	4.14	-7.91
	Cu <sup>2+</sup>	2.88 $\pm$ 0.02	2.81 $\pm$ 0.02	2.79 $\pm$ 0.02	2.77 $\pm$ 0.02	-7.98	25.99	-15.34
	Hg <sup>2+</sup>	1.63 $\pm$ 0.02	1.54 $\pm$ 0.02	1.33 $\pm$ 0.02	1.52 $\pm$ 0.01	-9.66	-4.91	-8.28
	Ni <sup>2+</sup>	2.97 $\pm$ 0.02	2.88 $\pm$ 0.01	2.69 $\pm$ 0.02	2.51 $\pm$ 0.02	-37.75	-78.84	-15.44
	Zn <sup>2+</sup>	2.84 $\pm$ 0.01	2.81 $\pm$ 0.02	2.77 $\pm$ 0.02	2.65 $\pm$ 0.01	-15.93	-2.90	-15.11

The  $\Delta G$  values for the present complexation reaction were negative for all the solvents indicating that the reaction was spontaneous and in most cases, both entropy and enthalpy factors were observed to be the dominating factor in making the  $\Delta G$  values negative. The change of standard free Gibbs energy values can be understood if ligand solvation is taken into consideration. In a strong solvating solvent such as DMF, the solvation of the metal ion (and probably that of the ligand) will be stronger than in solvents of lower solvating ability such as AN and MeOH. Therefore, it is necessary less energy for the desolvation step of the cation (and probably of the ligand) in the case of AN and MeOH than DMF and EtOH solutions [46].



**Fig. 5**  $\text{Log}K_f$  versus  $1000/T$  for  $M^{n+}$ -L complexes in AN solvent

#### 4. CONCLUSION

The stability constants and thermodynamic parameters of complexation reaction between the Schiff base ligand and metal cations of  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  in DMF, AN, EtOH, and MeOH solvents were measured at different temperatures using conductometric method. The obtained results in the current study demonstrated that the nature of the solvent system can affect the thermodynamic stability, stoichiometry, and selectivity of the complexes, and the obtained results indicated the formation of 1:1 and 2:1 (M:L) complexes in the solutions. The thermodynamic parameters indicated a spontaneous complex formation and the ability of the ligand to form stable complexes. The positive sign of the entropy and the negative sign of enthalpy are considered as a driving force for the complex formation.

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## بررسی واکنش کمپلکس شدن و ترمودینامیک یک لیگاند باز شیف جدید با برخی از یون های فلزی در حلال های غیر آبی به طریق هدایت سنجی

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### چکیده

واکنش کمپلکس شدن لیگاند باز شیف  $N-N'$  بیس (۵-برومو-۲-هیدروکسی بنزیلیدن)-۲،۲-دی متیل پروپان-۱،۳-دی آمین، با یون های فلزی  $Ag^+$ ،  $Cd^{2+}$ ،  $Co^{2+}$ ،  $Cu^{2+}$ ،  $Hg^{2+}$  و  $Ni^{2+}$  در حلال های استونیتریل، دی متیل فرمامید، اتانول و متانول در دماهای ۵، ۱۰، ۱۵ و ۲۵ درجه سانتیگراد، به روش هدایت سنجی بررسی شده است. ثابت های پایداری کمپلکس های  $ML$  و  $M_2L$  حاصل، از برازش رایانه ای داده های هدایت مولار برحسب نسبت مولی لیگاند به یون فلزی، در دماهای مختلف برآورد شد. گزینش پذیری لیگاند باز شیف برای کاتیون ها به ماهیت حلال بستگی دارد. در ۲۵ درجه سانتیگراد و در حلال استونیتریل، ترتیب پایداری کمپلکس های حاصل با یون های فلزی به ترتیب  $Ni^{2+} > Zn^{2+} > Co^{2+} > Cu^{2+} > Cd^{2+} > Ag^+ > Hg^{2+}$  است. نتایج نشان داد که پایداری کمپلکس های حاصل با توانایی حلال پوشی حلال، کاهش می یابد. مقادیر پارامترهای ترمودینامیکی ( $\Delta G^\circ$  و  $\Delta S^\circ$ ،  $\Delta H^\circ$ ) برای واکنش های کمپلکس شدن از وابستگی ثابت های پایداری (به دما، با استفاده از نمودارهای وانت هوف، برآورد شد. نتایج نشان داد که در بیشتر حالت ها، کمپلکس ها از نظر آنتالپی و آنتروپی پایدار می شوند.

### واژه های کلیدی

کمپلکس شدن؛ هدایت سنجی؛ ثابت های پایداری؛ بازهای شیف؛ پارامترهای ترمودینامیکی.