



Analysis of complexation between new bidentate bis-NHC ligand and some metal cations at different temperature

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ABSTRACT

In this research, the determination and complexation process between 3,3'-(2,2'-(4-methyl-phenylenesulfonamido)bis(ethane-2,1-diyl))bis(1-benzyl-3H-benzo[d]imidazol-1-ium)dibromide with Ni²⁺, Zn²⁺, Pd²⁺, Ag⁺, and Hg²⁺ cations in the binary mixture of methanol (MeOH) and water (H₂O) at different temperatures (15, 25, 35 and 45°C) were studied using a conductometric method. The results show that the stoichiometry of the complexes in all binary mixed solvents for Ni²⁺, Zn²⁺, and Pd²⁺ were 1:1 (M:L), while in other cases 1:2 (M:L) and 2:1(M:L). The stability constants (log K) of complex formation have been determined by fitting molar conductivity curves using a computer program (GENPLOT). The obtained data shows that in the pure methanol solvent system, the stability order is Ni²⁺<Pd²⁺<Zn²⁺<Hg²⁺<Ag⁺ and the complexation process seems more stable in pure methanol in most cases. The thermodynamic parameters (ΔG_c° , ΔH_c° , ΔS_c°) were determined conductometrically. The complexes in all cases were found to be enthalpy destabilized but entropy stabilized. The experimental data was tested by using an artificial neural network (ANN) program and was in good agreement with the estimated data.

1. Introduction

In early 1968, Wanzlick and Schönherr pioneered scientists that convey N-Heterocyclic carbene (NHC) complexation to a gained general acceptance among the researchers [1]. This effort was followed by Ardueng who found the stable crystalline carbene in 1991 [2]. In the meantime, numerous

studies have been reported with the various applications so far. NHCs ligands synthesized from benzimidazole and imidazole were founded as attractive ligands for complexation due to their structure variety and stability [3]. Generally, it is more stable than other types of carbenes, such as the Fisher and Schrock carbenes [4]. Furthermore, these types of ligands can bond to either hard and soft transition metal ions or atoms through strong chelation [5-9]. Several articles have described

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the interesting features of NHC ligands and their metal complexes in detail, especially on their C-C coupling catalysis activities [10-13]. Recently, its application as an anticancer activity was also reported [14-18]. Several bidentate bis-NHC ligands derived from benzimidazole and imidazole with a different bridging linker have been reported [19-23]. The types of bridging linkers play the main role in the coordination of metal complexes. Different types of bridging linkers will be offered for the different conformations of complexes. This is related to the flexibility, length, and size of linkers [5]. In addition, different cavity sizes of ligand, ionic radii of metal [24], and solvent systems are the important factors that can influence the stability of complexation formation [25].

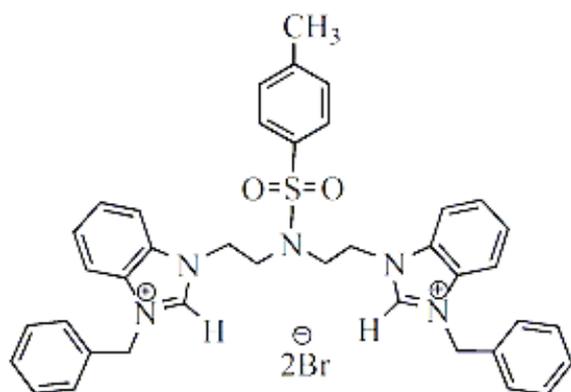


Fig. 1. 3,3'-(2,2'-(4-methyl-phenylenesulfonamido)bis(ethane-2,1-diyl))bis(1-benzyl-3H-benzo[d]imidazol-1-ium)dibromide, (NHCL)

To our certain knowledge, there have been few reports of the thermodynamic study of bidentate bis-NHC ligand complexes with different metal ions. This encouraged us to investigate the effects of pure and binary solvent mixtures on stability constants and thermodynamic parameters of complexes. In our study, bidentate bis-NHC ligand connected by sulfonamide moiety was designated and synthesized by a simple and efficient method [3, 19], namely 3,3'-(2,2'-(4-methyl-phenylenesulfonamido)bis(ethane-2,1-diyl))bis(1-benzyl-3H-benzo[d]imidazol-1-ium)dibromide (NHCL) (Fig. 1). To

determine the stability, selectivity and stoichiometry of NHCL-M^{n+} complexes with different metal cations, the conductometric technique was chosen [26]. This technique has several advantages such as great sensitivity [27], low cost [28] as well as simple experimental arrangement [29] compared with other techniques such as spectrophotometry, calorimetry [30], and NMR spectroscopy [31], and potentiometry [32-35]. The sensors based on electrochemical methods have been used to measure the analyte concentrations in water samples. Hence, electroanalytical techniques such as, potentiometry, voltammetry, and conductometry have been extensively reported. Other techniques such as inductively coupled plasma mass spectrometry [36], co-precipitation [37], flame atomic absorption spectrometry (F-AAS) [38], inductively coupled plasma optical emission spectrometry (ICP-OES) [39], and electrothermal atomic absorption spectrometry (ETAAS) [40] have also been used for the determination cations in water samples after complexation process. Thus, this study can contribute to a better understanding of ligand character and behavior in coordination chemistry, and the solvent effect in its complexation process.

2. Experimental

2.1. Chemicals and Instruments

The chemicals and metal ions used, which are nickel acetate, zinc acetate, palladium acetate, silver acetate, and mercury nitrite were purchased from Sigma-Aldrich (USA) and MERCK (Germany). All chemicals were analytical grade and used without further purification. Deionized distilled water and methanol with HPLC grade available from MERCK (Germany) were used as a solvent. The conductometric measurements were carried out using a digital Thermo Scientific conductivity device in a JULABO F12 thermostat water bath with a constant temperature maintained within $\pm 0.01^\circ\text{C}$. A conductometric cell model Orion 013005MD with a cell constant of 0.99cm^{-1} was used throughout the studies.

2.2. Synthesis of the bidentate bis-NHC ligand, NHCL

Several steps synthesized NHCL (4) from the diol (1) are shown in Figure 2. The synthesis of compounds (2) and (3) has been reported previously [19]. NHCL (4) was prepared according to the modification method designated as follows [3]. Benzyl bromide (0.1710 g, 1.0 mmol) was stirred in 20 ml of 1,4-dioxane, and then compound (3) (0.2296 g, 0.5 mmol) was added to it. The reaction mixture was refluxed at 100 °C for 12 hours and the pale yellow precipitated was obtained. The product was collected by filtration, washed with fresh 1,4-dioxane (2×5 mL) and diethyl ether (2×5 mL) and dried in vacuo to give a pale yellow powder (4).

2.3. Analysis procedure

These experimental designs were prepared according to the altered procedure [41-43] and were applied to all metal cations; Ni²⁺, Zn²⁺, Pd²⁺, Hg²⁺, and Ag⁺. The formation constant of the complexes will be obtained by using the procedure designated as follow. A solution of the metal ion

with a concentration, of 5.0×10^{-5} M was prepared and fixed in a titration cell. After that, the *L* with concentration 2.5×10^{-3} M was added to the titration cell using a micropipette. During the reaction, the desired temperature was fixed and a magnetic stir has been used to form a homogenized condition in the titration cell. The conductivity values were measured before and after each titration of ligands solution. The procedure was repeated for all metal cations in the MeOH-H₂O binary system (mol MeOH; 0.00, 9.99, 22.66, 39.73, 63.72 and 100.00%) at different temperatures (15, 25, 35 and 45°C).

3. Results and discussion

The general reaction for complex formation (1:1) can be stated by Equation 1 and the corresponding equilibrium constant (K_f), is given by Equation 2.



$$K_f = \frac{[NHCLM^{n+}]f_{(NHCLM^{n+})}}{[M^{n+}] [NHCL]f_{(M^{n+})}f_{(NHCL)}} \quad (\text{Eq.2})$$

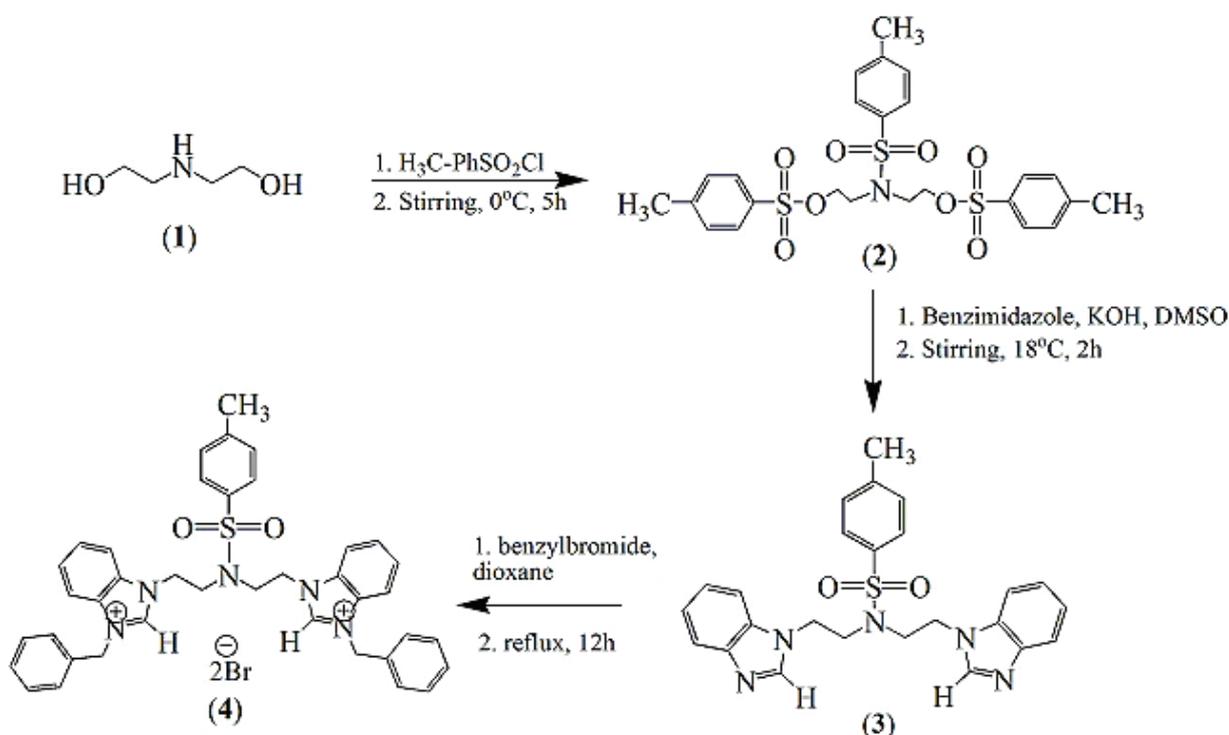


Fig. 2 . Synthesized scheme for NHCL (4).

The equation represents the equilibrium molar concentration of the complex $[NHCLM^{n+}]$, the free cation $[M^{n+}]$, the free ligand $[NHCL]$, and the activity coefficients of the species, f . Since the dilute condition was used in this work, the activity coefficient of the uncharged ligand, $f_{(NHCL)}$ is reasonably assumed to be unity. Dilute condition is where the ionic strength is less than 0.001 M. Based on the Debye-Hückel limiting law of electrolytes leads to the conclusion that $f_{(NHCLM^{n+})} \cong f_{(M^{n+})}$. Thus, the above equation can be simplified as Equation 3 [44].

$$K_f = \frac{[NHCLM^{n+}]}{[M^{n+}][NHCL]} \quad (\text{Eq.3})$$

The specific conductivity (K) in each point of the titration process is the value of the combination of conductivity of both metal salts, $K_{(M^{n+})}$ and $NHCLM^{n+}$ complex, $K_{(NHCLM^{n+})}$ which can be seen in the following Equation 4.

$$K = K_{(M^{n+})} + K_{(NHCLM^{n+})} \quad (\text{Eq.4})$$

Equations 5, 6 and 7 show the molar conductance of metal salt before the addition of NHC ligand, $\Lambda_{(M^{n+})}$, molar conductance of $NHCLM^{n+}$ complex, $\Lambda_{(NHCLM^{n+})}$ and observed molar conductance during titration, Λ_{Obs} .

$$\Lambda_{(M^{n+})} = \frac{K_{(M^{n+})}}{[M^{n+}]} \quad (\text{Eq.5})$$

$$\Lambda_{(NHCLM^{n+})} = \frac{K_{(NHCLM^{n+})}}{[NHCLM^{n+}]} \quad (\text{Eq.6})$$

$$\Lambda_{Obs} = \frac{K}{[M^{n+}]_t} \quad (\text{Eq.7})$$

where the total analytical concentration of the metal cations $[M^{n+}]_t$ is sum of the concentration of metal salts, $[M^{n+}]$ and $NHCLM^{n+}$ complex, $[NHCLM^{n+}]$ as shown in Equation 8.

$$[M^{n+}]_t = [M^{n+}] + [NHCLM^{n+}] \quad (\text{Eq.8})$$

By combining and simplifying the Equations 4, 5, 6

and 7, the following Equation 9 is obtained.

$$\begin{aligned} \Lambda_{Obs}[M^{n+}]_t &= \\ \Lambda_{(M^{n+})}[M^{n+}] + \Lambda_{(NHCLM^{n+})}[NHCLM^{n+}] & \end{aligned} \quad (\text{Eq.9})$$

Then, the observed molar conductance of the solution can be represented as Equation 10 by substituting of Equation 3 to Equation 9.

$$\begin{aligned} \Lambda_{Obs}[M^{n+}]_t &= \\ \Lambda_{(M^{n+})}[M^{n+}] + \Lambda_{(NHCLM^{n+})}K_f[M^{n+}][NHCL] & \end{aligned} \quad (\text{Eq.10})$$

The Equation 11 can be obtained by combining Equations 3 and 8.

$$\begin{aligned} [M^{n+}]_t &= [M^{n+}] + K_f[NHCLM^{n+}][NHCL] = \\ [M^{n+}](1 + K_f[NHCL]) & \end{aligned} \quad (\text{Eq.11})$$

Thus, the observed molar conductance of solution can be simplified as Equation 12 by substituting Equation 11 into Equation 10.

$$\begin{aligned} \Lambda_{Obs} &= \\ \frac{[M^{n+}]\Lambda_{(M^{n+})} + K_f\Lambda_{(NHCLM^{n+})}[M^{n+}][NHCL]}{[M^{n+}](1 + K_f[NHCL])} &= \\ \frac{\Lambda_{(M^{n+})} + K_f\Lambda_{(NHCLM^{n+})}[NHCL]}{1 + K_f[NHCL]} & \end{aligned} \quad (\text{Eq.12})$$

In contrast, the total concentration of NHC ligand, $[NHCL]_t$ can be described as in Equation 13.

$$[NHCL]_t = [NHCL] + [NHCLM^{n+}] \quad (\text{Eq.13})$$

The substitution Equation 3 into Equation 13 will gave the following Equation 14.

$$[NHCL]_t = [NHCL] + K_f[M^{n+}][NHCL] = [NHCL](1 + K_f[M^{n+}]) \quad (\text{Eq.14})$$

Then, the combination of Equations 11 and 14 gave Equation 15:

$$[NHCL]_t = [NHCL] + \frac{K_f[M^{n+}][NHCL]}{1 + K_f[NHCL]} = \frac{[NHCL] + K_f[NHCL]^2 + K_f[NHCL][M^{n+}]_t}{1 + K_f[NHCL]} \quad (\text{Eq.15})$$

Rearranging Equation 15 gave Equation 16:

$$K_f[NHCL]^2 + (1 + K_f[M^{n+}]_t) - K_f[NHCL]_t[NHCL] - [NHCL]_t = 0 \quad (\text{Eq.16})$$

With obtaining of $[NHCLM^{n+}]$ and $[NHCL]_t$, the values of other species involved by using the appraised amount of the formation constants at the current iteration step of the program. Refinement of the parameters is continued until the sum-of-squares of the residuals between calculated and observed values of the conductance for all experimental points is minimized. The output of the program GENPLOT comprises refined parameters, the sum-squares and the standard deviation of the data [45]. For determination of the stability constants of complex formation between the NHC ligand and various metal cations, the conductometric method has been selected as the best method in numerous studies [25, 41, 46]. To study the complexation reaction of L with the Ni^{2+} , Zn^{2+} , Pd^{2+} , Hg^{2+} , and Ag^+ cations, the changes in molar conductivity (Λ_m) of the solution were supervised as a function

of molar ratio ($[NHCL]_t/[M^{n+}]_t$) of the proposed complex in pure MeOH, pure H_2O and in MeOH- H_2O binary mixtures (mol%) at different temperatures (15, 25, 35 and 45°C). The resulting Λ_m versus ($[NHCL]_t/[M^{n+}]_t$) plots for (A) Ni^{2+} in MeOH- H_2O binary system (mol% MeOH=39.73) and (B) Ag^+ cations in MeOH- H_2O binary system (mol% MeOH= 9.90) are presented in Figure 3.

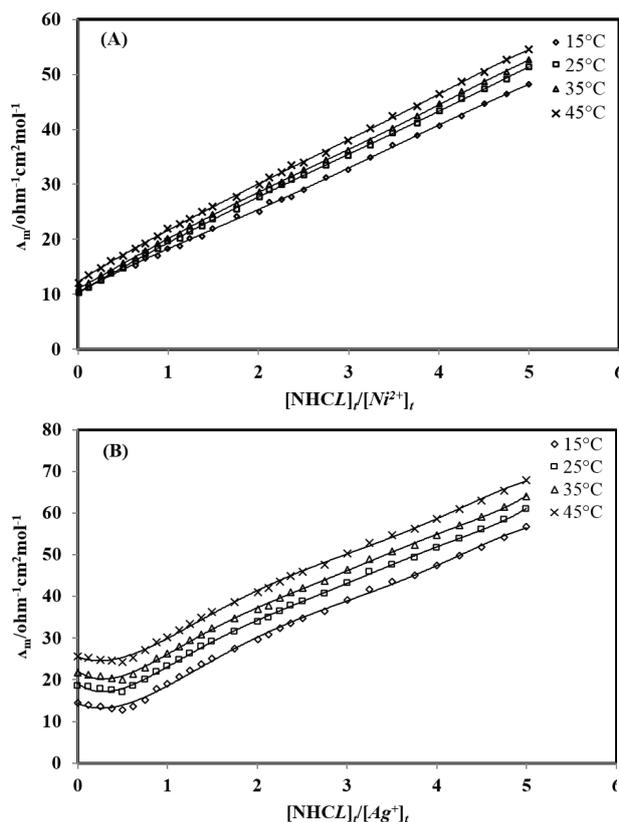
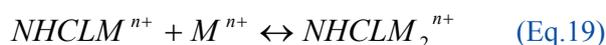


Fig.3. Molar conductance-mole ratio titration curves of (A) Ni^{2+} cation in MeOH- H_2O binary system (mol% MeOH=39.73), (B) Ag^+ cation MeOH- H_2O binary system (mol% MeOH=9.90) with NHCL at different temperatures.

As can be seen in Figure 3 (A), the Λ_m versus ($[NHCL]_t/[M^{n+}]_t$) plots for Ni^{2+} cation show an increase in Λ_m parallel to increase of the ligand concentration. This is corresponding to the free solvated metal ion is less mobile compared to the both ligand and complex. The same cases also happened to Zn^{2+} and Pd^{2+} slope, respectively. The slope for Ni^{2+} , Zn^{2+} , and Pd^{2+} shows that the

stoichiometric for these complexation reactions was 1:1 [M:NHCL]. While, from the Λ_m versus $([NHCL]_t/[M^{n+}]_t)$ plots for Ag^+ cation, Figure 3 (B) observed a slightly decreasing in Λ_m with increasing the ligand concentration, which indicated that ligand mobility is less than free solvated metal cation. However, it shows the increment after breaking points. This is indicated that the mobility of complexes in MeOH-H₂O binary mixtures is greater than free solvated cations [46]. The Λ_m versus $([NHCL]_t/[M^{n+}]_t)$ plots for Hg^{2+} also gave the same results as Ag^+ . It seems that in both complex formations, further addition of ligand to metal cation solution results in the formation of 1:2 [M:NHCL] and 2:1 [M:NHCL] complexes. Therefore, the general mechanism for all complexation processes may suggest as follows (Eq.17-Eq.19):



The formation constant values ($\log K_f$) of complexes for all cations were determined using a non-linear least-squares curve fitting program, GENPLOT from the corresponding Λ_m versus $([NHCL]_t/[M^{n+}]_t)$ plots at different temperatures. The obtaining data was summarized in Table 1.

The results in Table 1 show the increase of stability constants ($\log K_f$) for $NHCLM^{n+}$ complexes with an increase of temperature in most of the solvent systems. This is an indication for an endothermic complexation reaction between ligands and metal cations in the solution [36]. The obtained data shows that in the pure MeOH solvent system the stability constant is varying as $Ni^{2+} < Pd^{2+} < Zn^{2+} < Hg^{2+} < Ag^+$ and in the most cases complexation process seems more stable in pure MeOH. The results proved that the stability of the resulting complexes was influenced by the nature of the solvent system. In the reaction mixture solution, the ligand should

be able to excess metal cations which are solvated by solvent molecules to form a complex. Hence, dissimilarities in the nature of the solvent system may influence in the binding properties of NHCL, and subsequently, the stability and selectivity metal complexes.

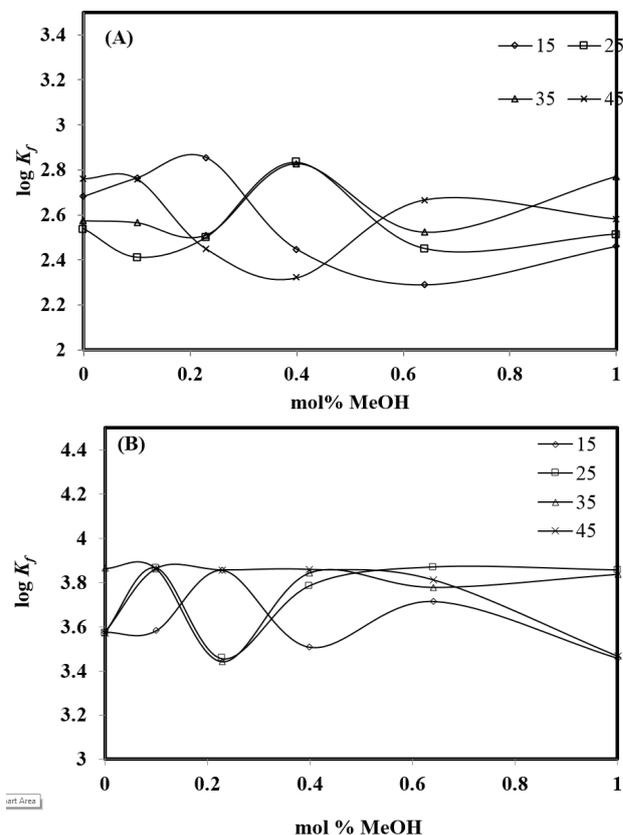


Fig. 4. Stability constant ($\log K_f$) of complexes in MeOH-H₂O binary system (mol% MeOH; 0.00, 9.99, 22.66, 39.73, 63.72 and 100.00%) at different temperature ($\diamond = 15^\circ C$, $\square = 25^\circ C$, $\Delta = 35^\circ C$, $\times = 45^\circ C$). (A) for Pd^{2+} cation and (B) for Ag^+ cation.

In the most cases, the changes in stability constant ($\log K_f$) of the complexes versus the composition of the MeOH-H₂O binary systems at various temperatures are not linear as shown in Figure 4. This pattern is probably due to solvent-solvent interaction that changed the structure of the solvent mixtures and consequently changed the solvation properties of the metal ions, ligand and the resulting complexes [25, 41]. In other cases, the increments of the stability constant value by the reducing of mol% of MeOH have been observed.

Table 1. $\log K_f$ value of $\text{NHCLM}^{\text{m+}}$ in $\text{MeOH-H}_2\text{O}$ binary mixtures at different temperatures for the studied metals cations.

Medium ^a / Ni ²⁺	$\log K_f \pm SD^b$			
	15°C	25°C	35°C	45°C
Pure MeOH	2.50 ± 0.14	2.43 ± 0.10	2.47 ± 0.07	2.48 ± 0.22
36.27% H_2O -63.72%MeOH	2.49 ± 0.31	2.46 ± 0.31	2.56 ± 0.27	2.40 ± 0.36
60.27% H_2O -39.73%MeOH	2.42 ± 0.19	2.57 ± 0.07	2.51 ± 0.08	2.46 ± 0.08
77.34% H_2O -22.66%MeOH	2.46 ± 0.08	2.55 ± 0.08	2.64 ± 0.07	2.45 ± 0.18
90.10% H_2O -9.90%MeOH	2.35 ± 0.31	2.60 ± 0.10	2.45 ± 0.12	2.85 ± 0.10
Pure H_2O	2.49 ± 0.08	2.56 ± 0.14	2.77 ± 0.08	2.45 ± 0.09
Medium^a/ Zn²⁺				
Pure MeOH	2.55 ± 0.08	2.76 ± 0.08	2.76 ± 0.08	2.75 ± 0.08
36.27% H_2O -63.72%MeOH	2.43 ± 0.14	2.40 ± 0.15	2.55 ± 0.08	2.56 ± 0.10
60.27% H_2O -39.73%MeOH	2.41 ± 0.16	2.43 ± 0.13	2.43 ± 0.15	2.45 ± 0.12
77.34% H_2O -22.66%MeOH	2.48 ± 0.11	2.42 ± 0.13	2.55 ± 0.07	2.57 ± 0.07
90.10% H_2O -9.90%MeOH	2.55 ± 0.12	2.64 ± 0.06	2.27 ± 0.32	2.86 ± 0.11
Pure H_2O	c	c	c	c
Medium^a/ Pd²⁺				
Pure MeOH	2.46 ± 0.21	2.51 ± 0.39	2.77 ± 0.17	2.58 ± 0.27
36.27% H_2O -63.72%MeOH	2.29 ± 0.31	2.45 ± 0.29	2.52 ± 0.17	2.67 ± 0.19
60.27% H_2O -39.73%MeOH	2.45 ± 0.21	2.83 ± 0.15	2.82 ± 0.13	2.32 ± 0.25
77.34% H_2O -22.66%MeOH	2.86 ± 0.10	2.50 ± 0.10	2.51 ± 0.09	2.45 ± 0.19
90.10% H_2O -9.90%MeOH	2.77 ± 0.08	2.41 ± 0.14	2.57 ± 0.08	2.76 ± 0.07
Pure H_2O	2.68 ± 0.17	2.54 ± 0.18	2.57 ± 0.19	2.76 ± 0.20
Medium^a/ Hg²⁺				
Pure MeOH	3.85 ± 0.12	3.86 ± 0.11	3.86 ± 0.12	3.85 ± 0.12
36.27% H_2O -63.72%MeOH	3.27 ± 0.35	3.42 ± 0.24	3.41 ± 0.25	3.46 ± 0.22
60.27% H_2O -39.73%MeOH	3.45 ± 0.21	3.82 ± 0.26	3.84 ± 0.21	3.84 ± 0.21
77.34% H_2O -22.66%MeOH	3.88 ± 0.12	3.45 ± 0.22	3.44 ± 0.30	3.43 ± 0.31
90.10% H_2O -9.90%MeOH	c	c	c	c
Pure H_2O	c	c	c	c
Medium^a/ Ag⁺				
Pure MeOH	3.46 ± 0.38	3.86 ± 0.20	3.84 ± 0.20	3.47 ± 0.40
36.27% H_2O -63.72%MeOH	3.71 ± 0.19	3.87 ± 0.22	3.78 ± 0.24	3.81 ± 0.23
60.27% H_2O -39.73%MeOH	3.51 ± 0.27	3.79 ± 0.22	3.84 ± 0.20	3.86 ± 0.17
77.34% H_2O -22.66%MeOH	3.85 ± 0.17	3.46 ± 0.32	3.44 ± 0.34	3.86 ± 0.17
90.10% H_2O -9.90%MeOH	3.86 ± 0.23	3.58 ± 0.32	3.86 ± 0.22	3.86 ± 0.22
Pure H_2O	3.58 ± 0.29	3.57 ± 0.29	3.57 ± 0.29	3.86 ± 0.22

^aComposition of binary mixtures is expressed in mol% for solvent system,^bSD = Standard deviation,^cThe data cannot be fitted to the equation in GENPLOT.

These results can be explained by the Gutmann acceptor-donor number effect. In this study binary mixture of MeOH-H₂O has been used. Pure solvent MeOH and H₂O have acceptor numbers 41.5 and 54.8 kcal mol⁻¹, respectively [47]. Therefore, the complexation in the solvent with lower acceptor ability will increase the stability constant value. This is due to the less competition of the ligand with the solvent molecules for the metal ions, thus increase the stability in the formation of complexes. The effect of a Gutmann donor number of solvents and their mixtures in this study is negligible because of their approximately equal value (DN_{Water} = 18 kcal/mol; DN_{MeOH} = 19 kcal/mol). By ignoring this parameter, the dielectric constant

of solvents, ϵ , plays another important role in the stability constants of complexes. According to the previous studies, the interaction between the oppositely charged ions in the solvent with low dielectric constant (Methanol, ϵ =32.6), in compared to water (ϵ =81.7), would be increased and cause to form the complexes. In order to better understand the complexation proceed discussed, it is useful to consider the enthalpy and entropy contribution to these reactions. The ΔH_c° and ΔS_c° parameters were estimated according to the van't Hoff plots that shows the corresponded $\ln K_f$ temperature data according to the van't Hoff's equation. All the van't Hoff plots of $\ln K_f$ versus $1000/T$ for all different metal cations, were constructed individually. Several cases were shown in Figure 5.

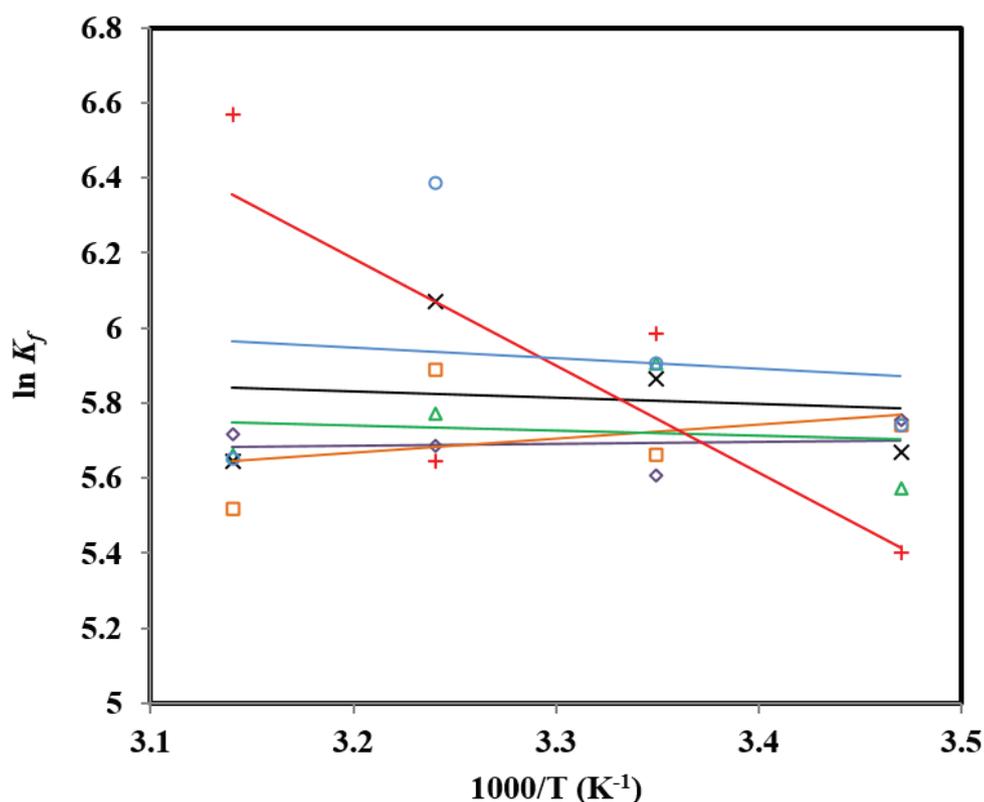


Fig. 5. Van't Hoff plot for $L-M^{n+}$ with Ni^{2+} cation in MeOH-H₂O binary system (mol% MeOH; ◇ = 100, □ = 63.72, △ = 39.73, X = 22.66, + = 9.90, ○ = 0.00) at different temperature.

The data demonstrated that these complexations process are temperature dependent. The value of standard enthalpy (ΔH_C°) for the complexation reaction was determined from the slope of the van't Hoff plots based on van't Hoff's equation

(Equation 20). Other thermodynamic parameters, the free energy of complex formation (ΔG_C°) and the value of the standard entropy (ΔS_C°) were obtained from thermodynamic relation Equation 21[39]. The calculated results are summarized in Table 2.

Table 2. Summary of thermodynamic parameters values of the NHCLMⁿ⁺ complexes in MeOH-H₂O binary mixture solvent.

Medium ^a /Ni ²⁺	$\log K_f \pm SD^b$		
	$\Delta G_C^\circ \pm SD^b$ (kJ.mol ⁻¹)	$\Delta H_C^\circ \pm SD^b$ (kJ.mol ⁻¹)	$\Delta S_C^\circ \pm SD^b$ (J.mol ⁻¹)
Pure MeOH	-13.9 ± 0.5	4.6 ± 1.0	62.1 ± 2.8
36.27% _{H₂O} -63.72% _{MeOH}	-14.04 ± 1.8	-5.6 ± 0.1	28.2 ± 1.9
60.27% _{H₂O} -39.73% _{MeOH}	-14.6 ± 0.4	-9.9 ± 0.3	16.0 ± 1.0
77.34% _{H₂O} -22.66% _{MeOH}	-14.5 ± 0.4	14.5 ± 0.4	97.3 ± 0.7
90.10% _{H₂O} -9.90% _{MeOH}	-14.8 ± 0.6	28.7 ± 0.3	146.1 ± 4.4
Pure H ₂ O	-14.6 ± 0.8	23.2 ± 7.4	127.0 ± 2.5
Medium^a /Zn²⁺			
Pure MeOH	-15.8 ± 0.5	11.0 ± 6.3	89.9 ± 2.0
36.27% _{H₂O} -63.72% _{MeOH}	-13.7 ± 0.9	7.3 ± 2.2	70.4 ± 6.9
60.27% _{H₂O} -39.73% _{MeOH}	-13.8 ± 0.7	1.1 ± 0.9	50.0 ± 1.6
77.34% _{H₂O} -22.66% _{MeOH}	-13.8 ± 0.7	5.5 ± 0.3	64.7 ± 2.2
90.10% _{H₂O} -9.90% _{MeOH}	-15.1 ± 0.4	17.9 ± 1.7	110.7 ± 5.6
Pure H ₂ O	c	c	c
Medium^a /Pd²⁺			
Pure MeOH	-14.4 ± 2.2	6.9 ± 0.7	71.4 ± 7.0
36.27% _{H₂O} -63.72% _{MeOH}	-14.0 ± 1.7	21.0 ± 1.9	117.4 ± 3.3
60.27% _{H₂O} -39.73% _{MeOH}	-16.2 ± 0.8	32.3 ± 8.0	162.7 ± 6.3
77.34% _{H₂O} -22.66% _{MeOH}	-14.3 ± 0.6	-4.5 ± 4.0	32.9 ± 1.9
90.10% _{H₂O} -9.90% _{MeOH}	-13.8 ± 0.8	31.6 ± 2.9	152.3 ± 9.4
Pure H ₂ O	-14.7 ± 1.0	16.5 ± 4.0	104.6 ± 6.9
Medium^a /Hg²⁺			
Pure MeOH	-22.0 ± 0.6	-1.2 ± 0.2	69.8 ± 2.0
36.27% _{H₂O} -63.72% _{MeOH}	-19.5 ± 1.4	11.1 ± 0.9	102.6 ± 3.6
60.27% _{H₂O} -39.73% _{MeOH}	-21.8 ± 1.5	24.6 ± 7.6	155.6 ± 5.0
77.34% _{H₂O} -22.66% _{MeOH}	-19.7 ± 1.3	-2.3 ± 0.5	58.4 ± 4.0
90.10% _{H₂O} -9.90% _{MeOH}	c	c	c
Pure H ₂ O	c	c	c
Medium^a /Ag⁺			
Pure MeOH	-21.9 ± 1.1	32.1 ± 9.2	181.1 ± 6.4
36.27% _{H₂O} -63.72% _{MeOH}	-22.1 ± 1.8	21.7 ± 8.3	146.9 ± 7.3
60.27% _{H₂O} -39.73% _{MeOH}	-21.6 ± 1.3	28.3 ± 9.8	167.4 ± 3.7
77.34% _{H₂O} -22.66% _{MeOH}	-19.3 ± 1.9	35.9 ± 3.5	185.1 ± 8.4
90.10% _{H₂O} -9.90% _{MeOH}	-20.4 ± 1.3	-0.2 ± 0.1	67.8 ± 4.2
Pure H ₂ O	-20.4 ± 1.3	-4.8 ± 4.5	52.3 ± 4.5

^aComposition of binary mixtures is expressed in mol% for solvent system,

^bSD = Standard deviation,

^cThe data cannot be fitted to equation.

$$\ln K_f = \frac{\Delta_f S_C^\circ}{R} - \frac{\Delta_f H_C^\circ}{RT}$$

(Eq.21)

$$\Delta G_{C,298.15}^\circ = \Delta H_{C,298.15}^\circ - T\Delta S_C^\circ$$

(Eq.21)

The results reveal, in the most cases the changes in ΔH_C° for the complexation process is negligible, whereas the change in ΔS_C° is significant. Therefore, the formation of complexes between ligand (NHCL) and all cations in MeOH-H₂O binary solvent mixtures are enthalpy destabilized but entropy stabilized. Additionally, the different solvent-solvent interaction in all solvent system and

changes in flexibility of ligand during complexation contribute to change in entropy. The calculated value of ΔG_C° in all cases shows negative values. This is an evidences that the ability of the ligand to form stable complexes with metal cations and the process were spontaneous [42]. However, The exitance of such a compensating e-ect between ΔH_C° and ΔS_C° values for all studied binary systems is shown in Figure 6. It is clear that the observed increase or decrease in ΔH_C° value which is depending on the nature of the metal ion will be compensated by an increase (or decrease) in the corresponding ΔS_C° value. Then the small changes of ΔG_C° values will be resulted due to this compensating e-ect for ΔH_C° and ΔS_C° , independently.

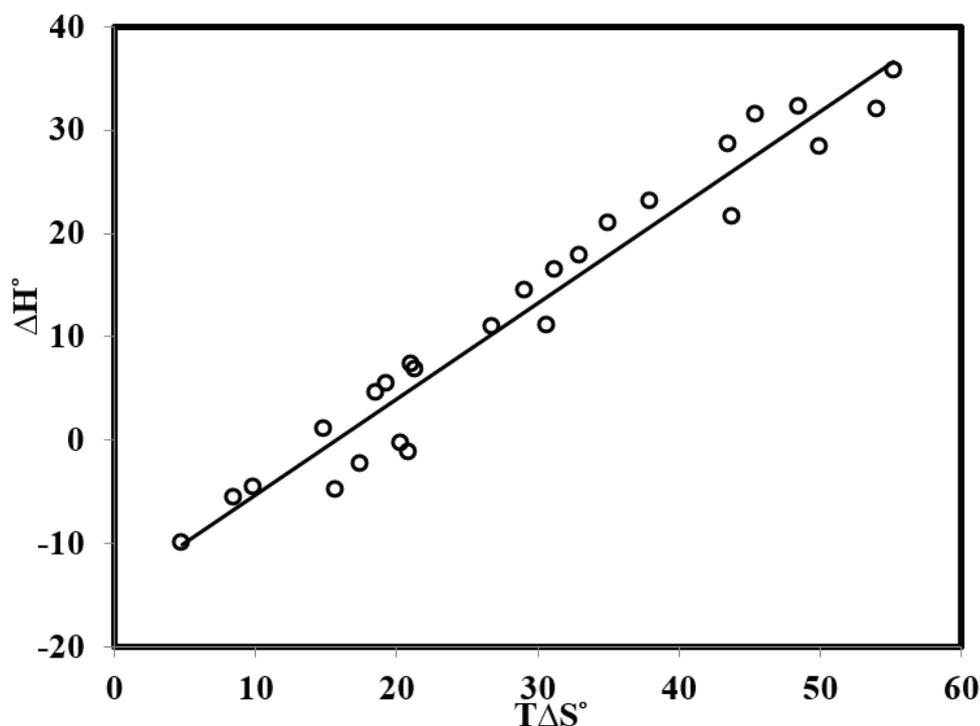


Fig. 6. Plot of ΔH_C° (kJmol⁻¹) versus $T\Delta S_C^\circ$ (kJmol⁻¹) for NHCLMⁿ⁺ (M= Ni²⁺, Pd²⁺, Zn²⁺, Hg²⁺ and Ag⁺) in different MeOH-H₂O systems (R²=0.9537).

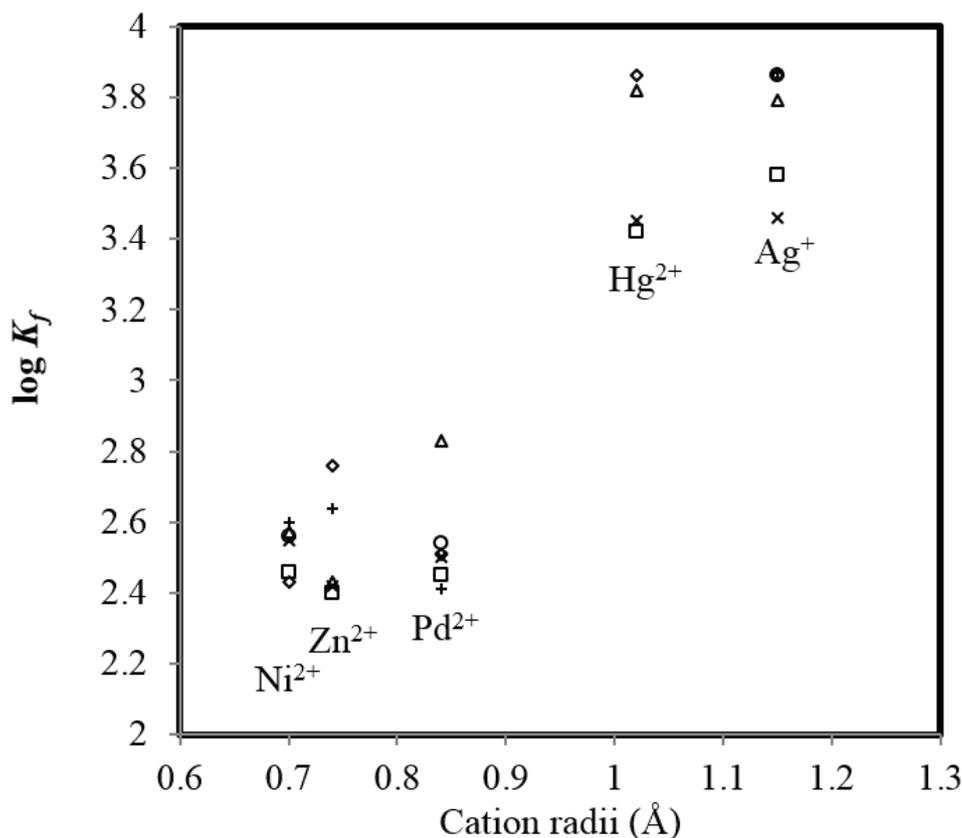


Fig. 7. Changes of stability constant ($\log K_f$) of NHCL- M^{n+} with all metal cation in MeOH- H_2O binary system (mol% MeOH; $\diamond = 100$, $\square = 63.72$, $\Delta = 39.73$, $\times = 22.66$, $+ = 9.90$, $\circ = 0.00$) at 25°C.

The variation of $\log K_f$ for all complex cases in contrast with cationic radius for studied cations in MeOH- H_2O binary mixture at 25°C were presented in Figure 7. As it is seen in Figure 7, the stability constant of complexes increase as the size of a metal cation increases from Ni^{2+} to Ag^+ . These results can be explained due to solvent system effect. Usually the small metals cations will be more solvated than the bigger metals cations in a same solvent system and decrease its mobility. Consequently, the competition ligand with solvent molecules was increase and resulted in the decreasing of stability constant [44].

3.1. Computational study

With the purpose to elucidate the obtained experimental results, a density functional theory

(DFT) study was conducted. The DFT calculations were carried out with the GAUSSIAN 09 software package, with the B3LYP/LANL2DZ basis set. The binding energy ΔE in the complexation between NHCL and M^{n+} in MeOH pure solvent is defined by the following formula, Equation 22:

$$\Delta E = E_{NHCLM^{n+}} - (E_{M^{n+}} + E_{NHCL}) \quad (\text{Eq.22})$$

Where ΔE , $E_{NHCLM^{n+}}$, $E_{M^{n+}}$ and E_{NHCL} are binding energy, NHCL M^{n+} complex energy, free metal ion energy and NHCL energy, respectively [48]. The optimized structure of free and complexes NHCL with Zn^{2+} and Ag^+ was shown in Figure 8(A, B, C), respectively. While the calculated results of binding energies for all complexes in MeOH pure solvent were listed in Table 3.

It is clear from Table 3 that the binding energy

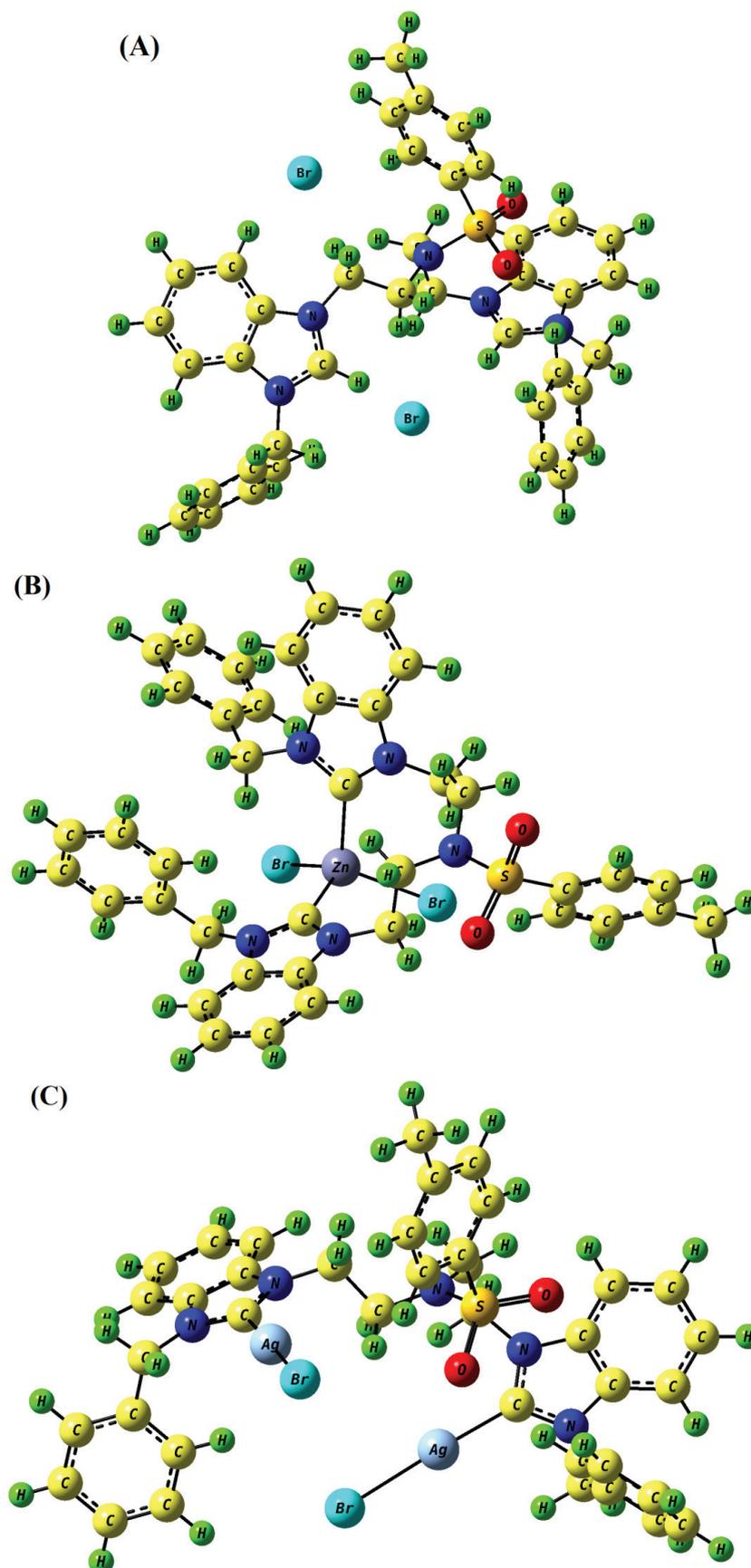


Fig. 8. Optimized structure of NHC ligand

Table 3. The calculated binding energies ΔE , in the formation of NHCLM^{n+} by DFT method, where E_{NHCL} is -1969.8454 (Hartree).

M^{n+}	E_M^{n+} (Hartree)	$E_{\text{NHCL-M}}^{n+}$ (Hartree)	ΔE (Hartree)	ΔE (kJ mol ⁻¹)
Ni ²⁺	-168.8263978	-2138.0707	0.66742646	1752.327917
Zn ²⁺	-65.30191723	-2034.37409	0.83955559	2204.252883
Pd ²⁺	-126.2368438	-2095.515285	0.63328753	1662.696169
Ag ⁺	-145.6275022	-2114.513658	1.02557279	2692.64097
Hg ²⁺	-42.5030206	-2011.502124	0.91262536	2396.097536

increases monotonically with increasing the size of studied cations. Therefore the binding energy of Ag^+ is much larger than other cations, showing prominent affinity to NHCL in the MeOH solvent. The obtained experimental data in MeOH pure solvent (Table 1) shows the same trends. As discussed before, small cations such as Ni^{2+} and Pd^{2+} have high solvation free energy with MeOH that causes them to be more solvalized in the solution, and have less interaction with free NHCL ligand.

3.2. Mathematical Modeling

Artificial neural network (ANN) as a mathematical (or computational) model that is inspired by the structure and function of biological neural

networks in the brain, is one of the most successful technologies in the last two decades [49-52]. In this research work, the ANN was applied for the simulation of property parameters correlation, and a good agreement in the experimental and predicted value is obtained. A 4-11-1 (input layer-hidden layer-output layer) network structure was used as shown in Figure 9. The effect of four parameters (cationic radii, temperature, molar percentage of MeOH in the media and molar percentage of water in the media) for the determining of complex formation (K_f) was the input layer matrix of the network. 59 training examples, 26 testing examples and 20 validating examples (10 times of each node) were prepared for training, testing and validating the network, respectively.

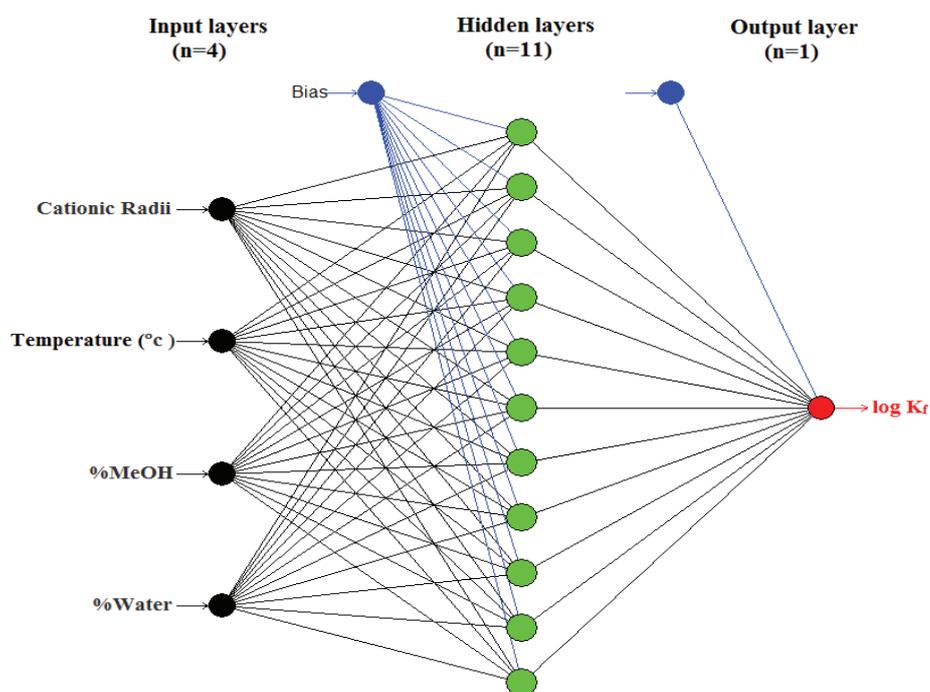


Fig. 9. Structure of neural network adopted in this study.

The model training based on the quick prob (QP) learning algorithm was carried out to test the data set and determine the minimum value of RMSE as an error function. The regression coefficient of

determination (R^2) showed a fairly good correlation between estimated and experimental data sets for both train (0.959) and test data sets (0.943) (Figure 10 (A) and (B)).

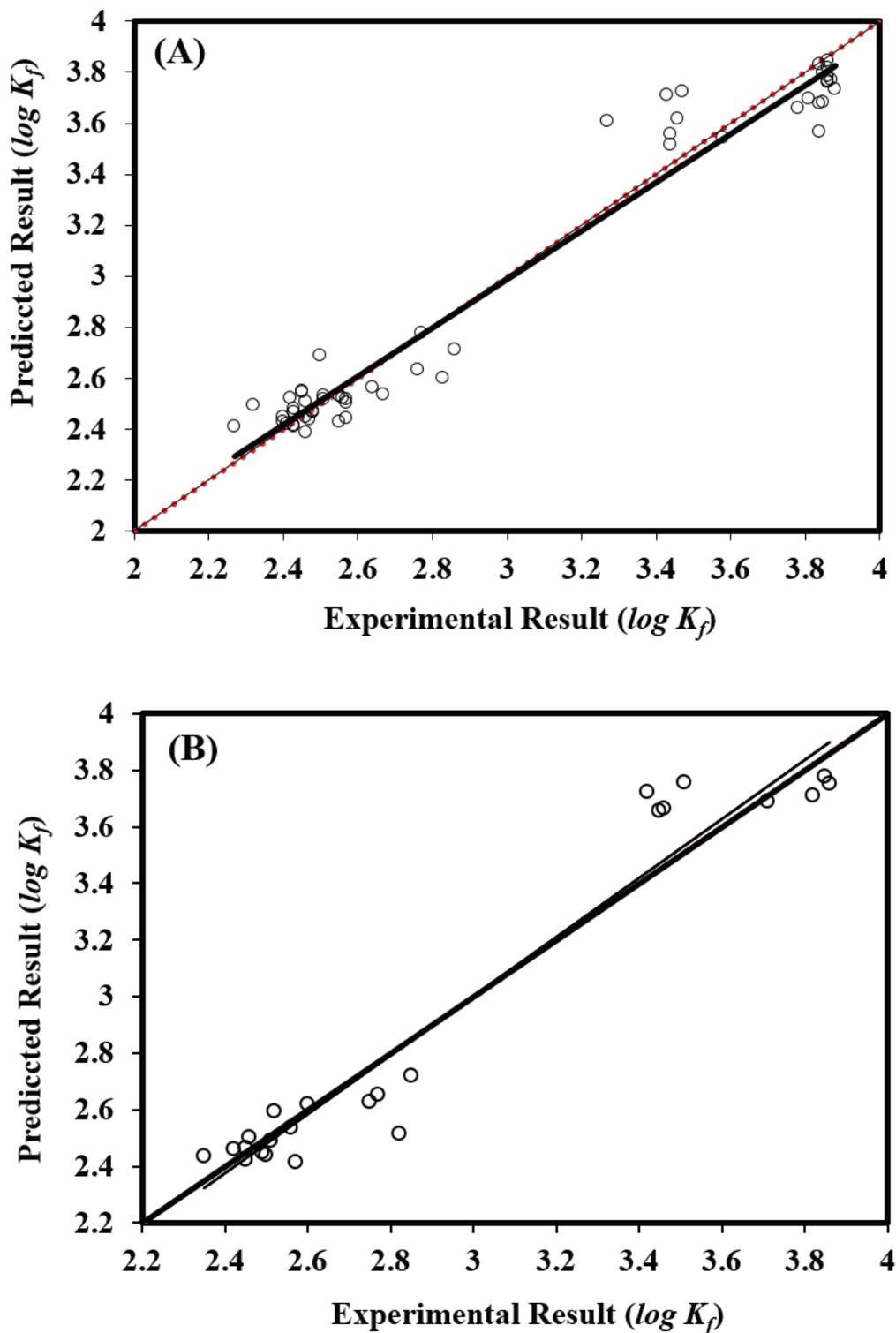


Fig. 10. Comparison of estimated $\log K_f$ with experimental data (a) training data set and (b) test data set.

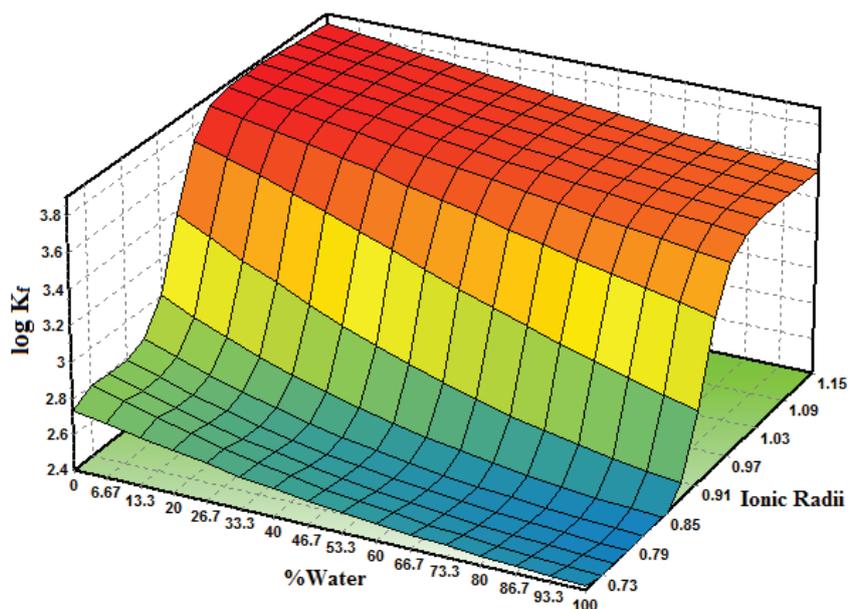


Fig. 11. Surface and contour plots of the stability constant ($\log K_f$) as a function of the mol% of water and ionic radius of cations (Ni^{2+} , Pd^{2+} , Zn^{2+} , Hg^{2+} and Ag^+)

The obtained constant formations of complex reactions between all metal studied cations and the proposed ligand using the various mole percentages of water in H_2O -MeOH binary media system at different temperatures were visualized in Figure 11 by drawing surface and contour plots of the stability constant ($\log K_f$) for the complex formation as a function of the mol% of H_2O in the binary mixtures and different studied cationic radius.

As seen in Figure 11, increasing of mol% of water and cationic radius causes a decrease and an increase in the constant stability of complexes ($\log K_f$). The maximum constant formation of complexes was obtained in zero mol percentage of water (100% of MeOH) and the highest amount of cationic radii related to Ag^+ cation (1.15Å). This result indicated that this model is valid for the estimation of constant stability of complexes of Ni^{2+} , Pd^{2+} , Zn^{2+} , Hg^{2+} and Ag^+ in MeOH-Water binary mixtures at different temperatures. The estimated results based on the ANN program were in a good agreement with obtaining experimental results.

4. Conclusion

According to the obtained results, the complexation of Ni^{2+} , Zn^{2+} , Pd^{2+} , Hg^{2+} and, Ag^+ cations with NHC

ligand can be explained in terms of the size-fit concept, where the NHC ligand forms a most stable complex with a cation having a size which fits best with its cavity size. The obtained data shows that in the pure MeOH solvent system the stability constant is varying as $\text{Ni}^{2+} < \text{Pd}^{2+} < \text{Zn}^{2+} < \text{Hg}^{2+} < \text{Ag}^+$ and the complexations process seems more stable in pure MeOH and pure H_2O . The result also showed that in most cases, the NHCLM^{n+} complexes was enthalpy destabilizer but entropy stabilizer. The stoichiometry of complexes for Ni^{2+} , Zn^{2+} , and Pd^{2+} are 1:1[M:NHCL]. While, for Hg^{2+} and Ag^+ , they have two stoichiometry which is 1:2[M:NHCL] and 2:1[M:NHCL]. The changes in the stability constant of the complex versus the composition of the MeOH- H_2O binary system at various temperatures are not linear in most cases. However, some results have shown that increment in stability is constant with the decrease of mol% MeOH in the solvent system. The effects of mole% of water and cationic radii of studied cations on the complexation reactions were investigated and high correlation between experimental data and ANN kinetic model was obtained which is a proof of the high performance of conductometric method for the complex formation study.

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Electronic Supplementary Material
(ESM: References 41-51)