Synthesis and Solution Complexation Studies of a new Schiff base Ligand

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ABSTRACT

A new Schiff base ligand, 2,2'-{pyridine-2,6-diylbis[nitrilo(E)methylylidene]}bis(4 bromophenol), has been synthesized by reaction of the 2,6-diamino pyridine with 5-bromo salicylaldehyde at ethanol under refluxing. The structure of the synthesized compound resulted from the IR, 1HNMR, MS and UV spectroscopy and elemental analysis data. Formation Constant (kf) value of it's complexes with Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+} and Hg^{2+} has been determined Conductometrically. The formation constants of the resulting 1:1 complexes have been calculated from the computer fitting of the molar conductance - mole ratio data at different temperatures. The stability of the complexes to vary in acetonitrile solvent was in the order of $Cu^{2+} > Cd^{2+} > Co^{2+} > Hg^{2+} > Ni^{2+}$. The enthalpy and entropy changes of the complexation reactions have been evaluated from the temperature dependence of formation constants.

Keywords: Conductometry; Complexation; Formation Constant; Synthesis; Schiff base; Ligand

INTRODUCTION

Schiff bases named after Hugo Schiff described the condensation between an aldehyde and an amine. Schiff base ligands are able to coordinate metals through imine nitrogen and another group usually linked to aldehyde. Schiff base are straightforward to prepare, monodentate electron donors with easily-tunable electronic and steric effect thus being versatile [1,2]. Schiff base ligands containing various donor atoms (like N, O, S etc.) show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities [3-5].

Pyridine derivative ligands are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful applications in biological, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [3, 6]. Not only have they played a seminal role in the development of modern coordination chemistry, but they

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can also be found at key points in the development inorganic biochemistry [7].

Coordination chemistry of these ligands with different metal to ligand ratio, results in different geometries, such as tetrahedral [8], square planner, pentagonal bipyramidal [9], or octahedral [10]. These organic ligands containing unsaturated nitrogen atoms can be regarded as soft Lewis bases [11].

The pyridine derivative ligands were chosen as suitable building blocks for complexation reaction with numerous transition metal ions, particularly those that can be regarded as soft Lewis acids such as Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+} and Hg^{2+}. These compounds are flexible about the central C=N bond. Each of these ligands contains five potential sites for coordination to metal ions.

Cobalt is an essential trace element for all animals, as the active center of coenzymes called cobalamins. These include vitamin B12 which is essential for mammals. Cobalt is also an active nutrient for bacteria, algae and fungi. Nickel, Cadmium and mercury are the most toxic among transition metals. They show the toxicity even in low doses to both plants and animals. Excess nasal and lung cancers are known to be associated with the refining of nickel [12]. Copper is an important trace element for plants and animals and is involved in mixed ligand complex formation in a number of biological processes. Copper complexes containing Schiff base ligands are of great interest since they exhibit numerous biological activities such as antitumor, anticandida [13], antimicrobial activities, etc.

In this work a new Schiff base, PDEAEBP (Figure 1) synthesized and formation constant (k_f) value of it's complexes with Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+} and Hg^{2+} has been determined Conductometrically. Also, we report the

enthalpy and entropy changes of the complexation reactions. To the best of our knowledge, this is the first reported research on thermodynamic study of PDEAEBP ligand using the conductometric method.

The findings from this paper can be used for many applications of pyridine derivative ligands, such as fabrication of ion selective electrode based on ionophores and solid phase extraction for determining toxic and heavy metal cation in real samples. Determination of ultra trace of these ions is usually carried out by flame [14] and graphite [15] atomic absorption spectrometry, as well as spectrophotometry [16], chemiluminescence [17] and electrothermal methods [18] after preconcentration. The most reliable methods used for the determination of toxic and heavy metal ions are the electrochemical methods, where they have many advantages such as high sensitivity and selectivity with high speed, less cost, relative simplicity and low detection limit.
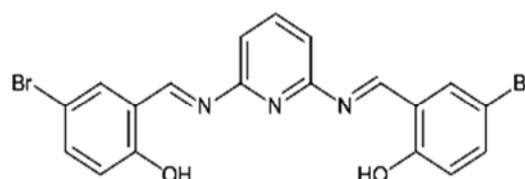
Fig. 1. Chemical structure of [PDEAEBP]**.**

EXPERIMENTAL

Chemicals

Spectroscopic grade acetonitrile and other organic solvents (all from Merck) was purified and dried by the previously described method [19]. The conductivity of the solvents was less than 1×10^{-6} S. cm-1. Analytical grade of nitrate salts of copper, cobalt, nickel, cadmium and mercury (all from Merck) were of the highest purity available. The new

synthesized PDEAEBP ligand with the highest purity was synthesized from 5-bromo salicylaldehyde and 2,6-diamino pyridine.

Instruments

Melting point was determined by use of a Barnstead Electrothermal 9200 apparatus and can be uncorrected. FT-IR spectra were performed on a JASCO 4200 spectrometer using KBr discs. NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts (ppm) were referenced to the internal standard tetramethylsilane (TMS). All UV-Vis Spectra recorded on a computerized double-beam 2550 Shimadzu spectrophotometer. The Mass spectrum was recorded on a Varian model Mat MS-311 spectrometer at 70 eV. Microanalyses were performed by the Elemental Analyzer (Elemental, Vario EL III) at the Tehran University.

All conductometric measurements were carried out by Metrohm 712 conductometer equipped with a Haake D1 circulator. In a typical experiment, 10.0 ml of metal ion solution (5.0×10^{-5} mol L^{-1}) in acetonitrile was placed in the two wall conductometer glass cell and the conductance of solution was measured. Then a known amount of the concentrated solution of PDEAEBP ligand in acetonitrile (5.0×10^{-3} mol L^{-1}) was added in a stepwise manner using an l0μl Hamilton syringe. The conductance of the solution was measured after each addition. The PDEAEBP ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

In all measurements, cell was thermostated at desired temperature ±0.1ºC; the cell constant at the different temperature used was determined by measuring the conductivity of 1×10^{-2} mol L^{-1} solution of analytical grade KCl in triply distilled deionized water. The

corresponding cell constant at 15º, 25º, 35º, and 45ºC were 0.834, 0.832, 0.829 and 0.820 cm^{-1} respectively. A dip-type conductivity cell made of platinum black have used.

Synthesis of PDEAEBP

A solution of 5-bromo salicylaldehyde (2 mmol), 2,6-diamino pyridine (1 mmol) in ethanol (10 mL) was refluxed for 2 h. The reaction mixture was cooled in an ice bath to give the precipitate. The crude product was collected, washed with water (5 mL) and then recrystallized from ethanol to give the pure Schiff bases.

Spectroscopic data of PDEAEBP

Yellow solid, Yield 81%, M.p. 227-229ºC, IR (KBr, υ_{max}): 3423 (OH), 3048 (C-H), 1607, 1542 (C=N), 1474, 1273 (C=C), 1168 (C-OH), 817 (C-Br) cm^{-1}; ^{1}H NMR (DMSO-d_6), δ: 6.25-8.10 (m, 7H, H-Ar), 9.30 (s, 2H, CH=N), 12.88 (s, 2H, OH) ppm; MS (m/z, %): 475 (M^+, 55), 460 (25), 291 (60), 277 (70), 201 (70), 201 (70), 94 (100); UV/vis λ_{max} (EtOH) 295, 316, 384 nm. Anal. Calcd. For $C_{19}H_{13}Br_2N_3O_2$: C, 48.03; H, 2.76; Br, 33.63; N, 8.84%. Found: C, 48.34; H, 2.73; Br, 33.57; N, 8.91.

Stability constants of ligand - metal ions complexes

The formation constant (k_f) and the molar conductance *vs* C_L/C_M mole ratio data, of the resulting 1:1 complexes between the PDEAEBP and different metal ions at various temperature were calculated by the KINFIT [20] program. Adjustable parameters are the k_f, molar conductance of free metal ion, and molar conductance of complex.

The free metal ion concentration, [M], was calculated by a Newton-Raphson procedure. When the value of [M] had been obtained, the concentration of all other species involved are calculated from

the mass balance equations by using the estimated value of the formation constant at the current interaction step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed molar conductance for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum of squares and the standards deviation of the data [21-23].

Thermodynamic parameters of ligand - metal ions complexes
In order to have a better understanding of the thermodynamics of complexation between PDEAEBP and metal ions in acetonitrile solvent, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy of the complexation reactions were determined by measuring the formation constants of the resulting ML complex as a function of temperature with Van't Hoff Equation (Equation 1).

$$2.303\log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (1)$$

RESULTS AND DISCUSSION

Synthesis *of PDEAEBP*
The Schiff base PDEAEBP is formed in good yield by the condensation of the 2,6-diamino pyridine and 5-bromo salicylaldehyde at ethanol under refluxing [24,25] (Scheme 1).
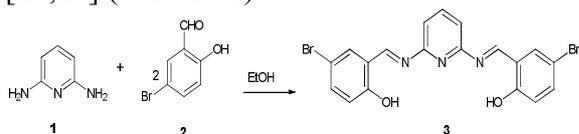
Scheme 1. Synthetic method for *PDEAEBP*

The structure of the Schiff base (PDEAEBP) was characterized by the spectroscopic data. The IR spectrum of the ligand shows a broad band at 3423 cm^{-1}, which can be attributed to the phenolic OH group. Phenolic C-O stretch band is observed at 1273 cm^{-1} in the Schiff base. However, the band due to the azomethine (C=N) group in this compound is observed at 1607 cm^{-1}. The ^{1}H-NMR spectra of synthesized compound is consistent with its structure. The ^{1}HNMR spectra of this compound is simple and consist of the aromatic proton signals and 2 singlet signals related to the resonance of the CH=N and OH proton, which appeared at 9.30 and 12.88 ppm, respectively. The aromatic protons resonate as a multiple signal at 6.25-8.10 ppm. The mass spectrum of this compound exhibited [M$^+$] at m/z 475 (55%) which elucidate the structure of the reaction product. The UV spectrum of the bis-Schiff base in ethanol, exhibited three absorption bands at 384, 316 and 295 nm assigned to $n{\rightarrow}\pi^*$, $\pi{\rightarrow}\pi^*$ and $n{\rightarrow}\sigma^*$ transitions, respectively.

Conductometric Studies
The molar conductance of the nitrate salts of Cd^{2+}, Cu^{2+}, Co^{2+}, Ni$^+$ and Hg^{2+} in acetonitrile solvent was monitored as a function of the PDEAEBP to metal ion mole ratio, and the stoichiometry of the complexes in acetonitrile solution, was examined by the mole ratio method at variable temperatures. A sample of the resulting plots for all metal ions complexes at 25ºC in acetonitrile solution, are shown in Figure 2. Mole ratio plots of PDEAEBP and it's complexes with Co^{2+} ions at various temperatures are shown in Fig. 3. It is evident that ML complexes are formed in solutions.

It was observed that the Λ value increases with an increase in [L]$_t$ / [M]$_t$ ratio for all the systems. This has been explained [26, 27], On the basis of a solvation sphere. The divalent metal ions have a high charge-to-radius ratio on

account of which they are highly solvated. But on complexation, the Schiff base molecule replaces the salvation sheath around the metal ion and as a result the moving entity becomes less bulky and more mobile. The curves show a break point at $[L]_t/[M]_t = 1$, which indicates the formation of 1:1 complexes between PDEAEBP and the metal ions.

M(solvated) + L = ML + solvent.
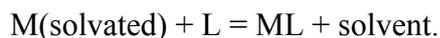
That is the equilibrium constant represents the stability of the complex relative to the stability of the solvent complex.
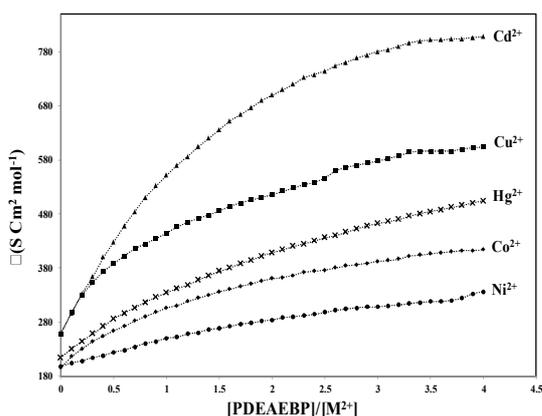
Fig. 2. Mole ratio plots of the metal ions (5.0 $\times 10^{-5}$ mol L^{-1}) with PDEAEBP ligand (5.0×10^{-3} mol L^{-1}) in Acetonitrile solution at 25°C.

The formation constants of the resulting ML complexes were obtained by molar conductance measurements of solutions in which varying concentrations of ligand (5.0×10^{-3} mol L^{-1}) were added to fixed amounts (5.0×10^{-5} mol L^{-1}) of metals ions solution. The entire resulting molar conductance-mole ratio data were further supports the formation of ML complexes in solution.

Various methods to calculate stability constants from measurements of properties

involving intrinsic factors, such as molar conductivity etc. have been described in the literature [23, 26]. When a ligand (L) forms a complex ($M_aL_b^{m+}$) with a cation (M^{m+}), the equilibrium equation can be written as:

$$a\,M^{m+} + b\,L \longleftrightarrow M_aL_b^{m+}$$
$$\alpha\,C_M\,C_L - (1-\alpha)\,C_M\,(1-\alpha)\,C_M$$
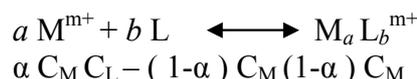
where M^{m+}, L, and α are the cation, ligand and fraction of free cations respectively. Thus the equilibrium constants k of different ratios of complex formation was calculated using the following equations:

$$K = [M_aL_b^{m+}] / [M^{m+}]^a\,[L]^b \qquad (2)$$
$$C_M / C_L = 1$$
$$C_M = [M_a^{m+}] + [M_aL_b^{m+}]$$
$$C_L = [L_b] + [M_aL_b^{m+}]$$

$[M_a^{m+}]$, $[L_b]$ and $[M_aL_b^{m+}]$, are the concentrations of uncomplexed action, uncomplexed schiff base and complexed cation, respectively.

$$\alpha = [M_a^{m+}] / C_M$$
$$P = [M_aL_b^{m+}] / C_M = K\,[L_b] / (1+K[L_b])$$

P, is the experimental mole fraction of the complexed cation or the ligand, and a and b are the complexing degrees of both sides in the case of several degrees of complexing. The observed conductivity, Ҡ, is given by:

$$Ҡ = Ҡ_{Ma}^{m+} + Ҡ_{MaLb}^{m+}$$

$Ҡ_{Ma}^{m+}$, $Ҡ_{MaLb}^{m+}$, are the observed conductivities of the electrolyte and the ligand compound-electrolyte complex, respectively. The molar conductivities are:

$$\Lambda_{MAm} = Ҡ_{MAa}^{m+} / [M_a^{m+}]$$
$$\Lambda_{MaLb}^{m+} = Ҡ_{MaLb}^{m+} / [M_aL_b^{m+}]$$

Λ_{Ma}^{m+} and Λ_{MaLb}^{m+} are the designated molar conductivities of the electrolyte and

the ligand compound-electrolyte complex, respectively [27].

$$\Lambda = \mathcal{K} / C_M$$
$$\Lambda = \alpha\Lambda_{Ma}^{m+} + (1-\alpha)\Lambda_{MaLb}^{m+} \qquad (3)$$

As a result of Eq. (2) and Eq. (3) can be transformed into:

$$K = (\Lambda_{Ma}^{m+} - \Lambda) / ((\Lambda - \Lambda_{MaLb}^{m+}) [L_b])$$

where $[L_b] = C_L - C_M.P$ and $[L_b] = C_L - C_M.(\Lambda_{Ma}^{m+} - \Lambda)/(\Lambda_{Ma}^{m+} - \Lambda_{MaLb}^{m+})$ and C_M, C_L are the total concentrations of metal ion and schiff base, respectively. Various quantum-chemical and force-field computations of crown ethers and of their metal complexes have been reported recently, even on the *ab initio* level [28, 29] and the density functional level of theory (DFT) [30-32].

For evaluation of the formation constants from molar conductance *vs.* C_L / C_M mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the molar conductance-mole ratio data for Ni^{2+} and PDEAEBP at $25°C$ is shown in Figure 4. The resulting k_f of the PDEAEBP complexes at $25°C$ are listed in Table 1.

All of the $\log k_f$ values evaluated from the computer fitting of the corresponding molar conductance-mole ratio data are listed in Table 1. Van't Hoff plots of $\log k_f$ *vs.* 1000/T, for metals complexes in methanol solution were linear and are shows in Figure 5. ΔH^0 and ΔS^0 values were determined from Van't Hoff Equation (Equation 1) in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also listed in Table 1.

Comparison of the data given in Table 1 indicate that the stability of the ML complexes to vary in the order $Cu^{2+}> Cd^{2+}> Co^{2+}> Hg^{2+}> Ni^{2+}$ in acetonitrile solution.
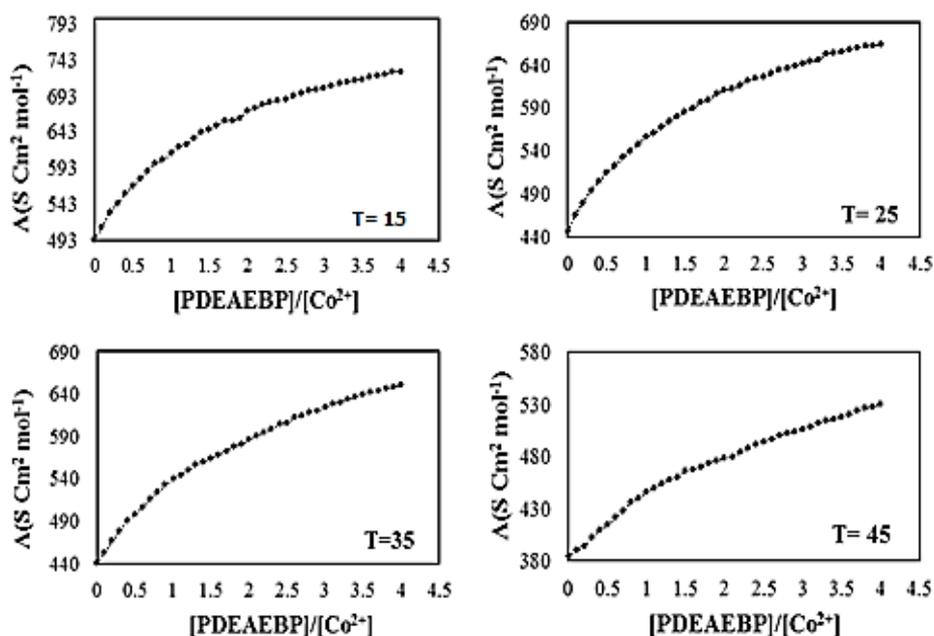
Fig. 3. Mole ratio plots of PDEAEBP and it's complexes with Co^{2+} ions in acetonitrile solution at various temperatures: $15°C$, $25°C$, $35°C$, $45°C$.
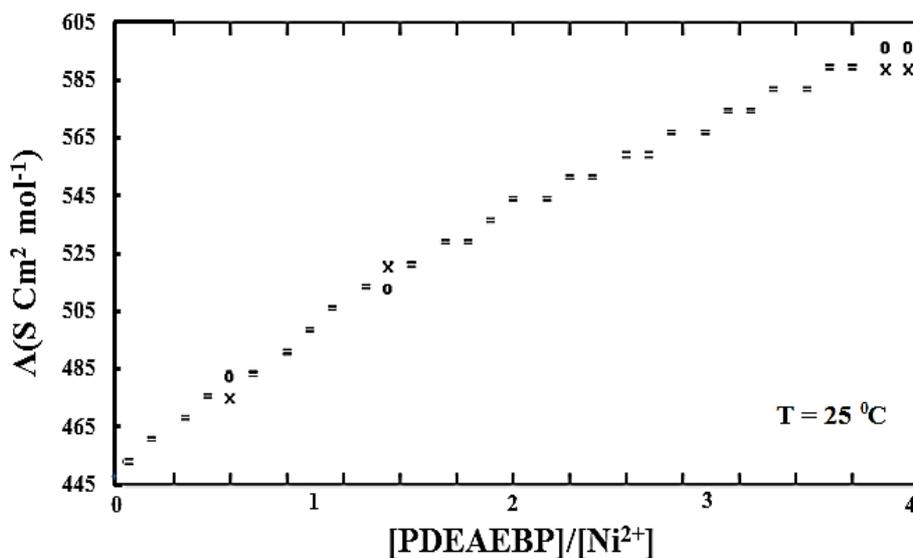
Fig. 4. Computer fit of molar conductance *vs*. [PDEAEBP]/[Ni^{2+}] mole ratio plot in acetonitrile at 25°C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

Table 1. Formation constants, enthalpies, and entropies for different M^{2+}(PDEAEBP) complexes in acetonitrile solution

cation	Log $K_f \pm$ SD				ΔH^0 (kj mol^{-1})	ΔS^0 (jmol^{-1}K^{-1})
	15°C	25°C	35°C	45°C		
Hg^{2+}	4.24 ± 0.01	3.99 ±0.01	3.75 ±0.02	3.40 ± 0.06	2.52±0.3	-4.5±0.1
Ni^{2+}	4.07 ± 0.01	3.69 ± 0.05	3.65 ± 0.05	3.30 ± 0.01	2.3±0.1	-4.0±0.5
Cd^{2+}	4.60 ± 0.04	4.35 ± 0.05	4.24 ± 0.01	4.17 ± 0.04	1.9±0.2	-1.9±0.5
Co^{2+}	4.38±0.01	4.33±0.06	4.20±0.01	4.13±0.01	0.9±0.1	1.6±0.3
Cu^{2+}	4.61±0.01	4.48±0.01	4.40±0.05	4.32±0.01	0.9±0.01	-.1±0.1
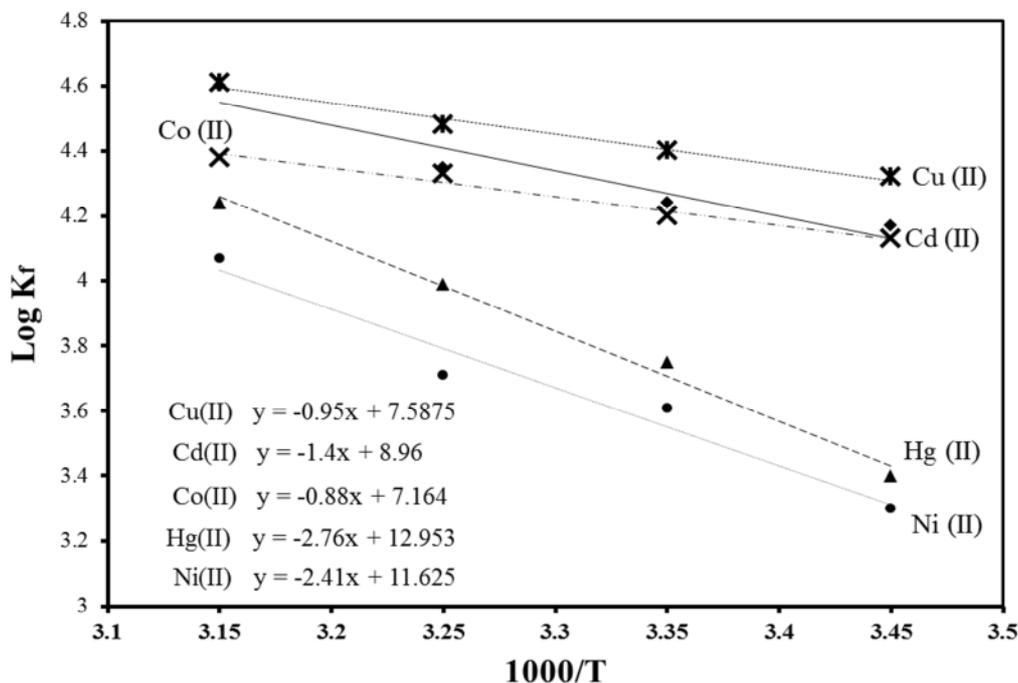
Fig. 5. logk$_f$ *vs*. 1/T for the ML metal ions complexes with PDEAEBP in acetonitrile solution.

CONCLUSION

The stability constant for the complexation of metallic ions with PDEAEBP in acetonitrile were determined conductometrically at different temperatures. According to the obtained results, the compression of the formation constant showed that in most of the cases, the stability constant of the complexes increased with the decreasing temperature. Determination of thermodynamic parameters showed the positive value and to prove the ability of the ligand to form stable complexes and the process trend to proceed spontaneously. Furthermore, the negative values, indicated that entropy was responsible for the complexing process in most of the cases.

The enthalpy and entropy changes are strongly solvent dependent, the observed increase (or decrease) in $\Delta H°$ value will be compensated by an increase (or decrease) in the corresponding $\Delta S°$ value.

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