Conductometric Studies of the Complexation of Zn²⁺, Cu²⁺, Co²⁺, Ni²⁺ and Cd²⁺ with Schiff Base Ligand in Acetonitrile Solution

Mahmood Payehghadr*, Ali Akbar Babaei† and Lotfali Saghatforoush‡

Department of Chemistry, Payame Noor University (PNU), Karaj, Iran
E-mail: mpayehghadr@pnu.ac.ir; mahmood_payehghadr@yahoo.com

The complex-formation reactions between Cu²⁺, Zn²⁺, Co²⁺, Ni²⁺ and Cd²⁺ ions with 4-nitro-2-[(2-(2-pyridin-2-yl-ethyl-solphanil)ethylymino)-methyl]phenol (PYTANO₂) Schiff base ligand, has been studied by conductometric method in acetonitrile at various temperatures. Formation constants of the 1:1 and 1:2 (metal ion to ligand) complexes were evaluated from computer fitting of the molar conductance-mole ratio data at different temperatures and found that complexes to vary in the order of Ni²⁺ > Co²⁺ > Zn²⁺ > Cu²⁺ > Cd²⁺. The enthalpy and entropy changes of the complexation reaction were determined from the temperature dependence of the formation constants.

Key Words: Conductometric, Formation constants, Schiff bases, Complexation.

INTRODUCTION

The condensation of an amine with an aldehyde, forming a Schiff base, is one of the oldest reactions in chemistry[1]. Schiff base ligands coordinate to a metal through the imine nitrogen and another group, usually oxygen, situated on the origin aldehyde. When a diamine was first combined with two equivalent of salicylaldehyde, the salen ligands came into being[2,3]. These ligands are quite familiar as tetradentate ligands in metal complexes[4-6]. These ligands with N₂O₂ donor atom set are well known to coordinate to inorganic and organic cations to give rise to chelate complexes[7]. Diamine Schiff bases are different from monoamine Schiff bases having two chromophores bridged by a methylene chain in a molecule and thus the mutual interactions between the chromophores appears to affect their chemical and physical properties[7]. Therefore interesting optical properties derived from the interaction between the two chromophores in the diamine Schiff bases could be expected. Some of optical properties of diamine Schiff base ligands have been reported in literature[8], but the complexation reaction of these complexes in nonaqueous solvents has not been reported. Schiff bases derived from salicylaldehyde (salens) as polydentate ligands are well known to form stable complexes with transition metal ions[9]. Salen complexes

†Department of Chemistry, Payame Noor University (PNU), Sary, Iran.
‡Department of Chemistry, Payame Noor University (PNU), Khoy, Iran.

of transition metals have been frequently used as catalysts in such diverse processes as oxygen and atom-transfer[10], enantioselective epoxidation[11], azidation[12], mediating organic redox reactions and recently as ionophores in ion-selective studies[13].

Since the nature of solvent may strongly influence the stoichiometry and complexation of transition metal complexes in solution, it is decided to study the complexation reaction and thermodynamic of a Schiff base ligand, PYTANO$_2$, (Fig. 1)[14] with some transition metal ions in acetonitrile solutions. In this paper, the conductometric study of the stoichiometry, complexation reaction and thermodynamics of PYTANO$_2$ Schiff base ligand with Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions in acetonitrile are reported.
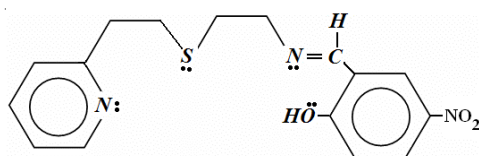

Fig. 1.   Schiff base ligand 4-nitro-2-[(2-(2-pyridin-2-yl-ethyl-solphanil)ethylymino) methyl]phenol (PYTANO$_2$)

EXPERIMENTAL

Reagent grade metals nitrates and acetonitrile (AN) all from Merck and recently synthesized PYTANO$_2$ Schiff base were of highest purity available and were used without any further purification.

Conductometric study: Conductometric measurements were carried out by Metrohm 712 conductometer equipped with a Haake D1 circulator. In a typical experiment, 10 mL of metal ion solution (5×10^{-5}-1×10^{-4} 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 Schiff base ligand in acetonitrile (5×10^{-3}-1×10^{-2} mol L^{-1}) was added in a stepwise manner using an l0 µL Hamilton syringe. The conductance of the solution was measured after each addition. The Schiff base ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

Stability constants of metal ions-ligand system: The formation constant ($K_\beta = K_1 + K_2$) of the resulting 1:1 and 1:2 (metal ion to ligand) complexes between the Schiff base and different cations at various temperatures were calculated by fitting the molar conductance (Λ) *versus* C_L/C_M mole ratio data evaluated with a non-linear least-squares program KINFIT[15].

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[16].

Thermodynamic parameters of metal ions-ligand system: In order to have a better understanding of the thermodynamics of complexation between Schiff base and metal ions in acetonitrile, 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 complexes as a function of temperature with Van't Hoff eqn. 1.

$$2.303 \log K_f = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{1}$$

RESULTS AND DISCUSSION

The molar conductance of the nitrate salts of Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} in acetonitrile solvent was monitored as a function of the $PYTANO_2$ to metal ion mole ratio and the stoichiometry of the complexes in acetonitrile was examined by the mole ratio method at variable temperaturs. A sample of the resulting plots for Zn^{2+} and Cu^{2+} ions complexes is shown in Fig. 2 and it is evident that ML and ML_2 complexes are formed in solution. As can be seen in acetonitrile solvent, addition of the ligand to the metal ions solutions cause a continuous increase in molar conductance of the solutions. This might indicate that the complexes formed are more mobile than the solvated metals ions. It is well known that transition metals ions strongly complexed with acetonitrile[17] and such a solvated ions are highly ordered and sluggish[18].
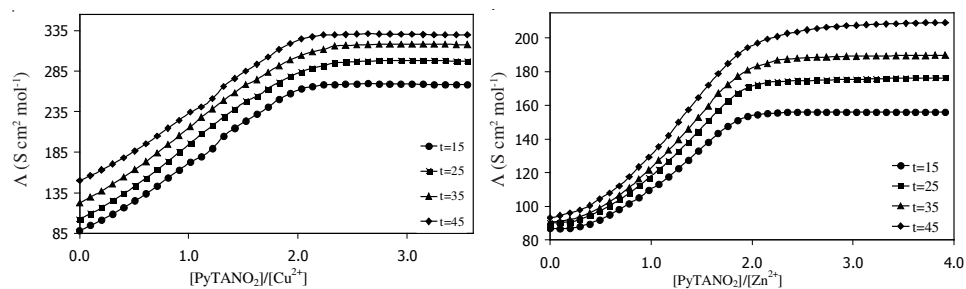

Fig. 2. Mole ratio plots of $PYTANO_2$ and it's complexes with Cu^{2+} and Zn^{2+} ions at various temperatures: (1) 15 °C, (2) 25 °C, (3) 35 °C, (4) 45 °C calculated points are the same within the resolution of the plot

The first addition of $PYTANO_2$ ligand formed complexes with metals ions resulting in a more mobile system with relatively high conductivity. Further additions of

ligand to the relatively mobile system caused a gradual increase in conductivity. However, the slope of the corresponding molar conductance-mole ratio plots change at the point where the ligand to ions ratio are one and further additions of the ligand cause no or very slight changes in the molar conductance. Such a conductance behavior is indicative of the formation of ML and ML_2 complexes in solutions.

The formation constants of the resulting complexes were obtained by molar conductance measurements of solutions in which varying concentrations of ligand $(5 \times 10^{-3} \text{ mol L}^{-1})$ were added to fixed amounts $(5 \times 10^{-5} \text{ mol L}^{-1})$ of metals ions solution. The entire resulting molar conductance-mole ratio data were best fitted to eqn. 1, which further supports the formation of mixed complexes in solution.

For evaluation of the formation constants from molar conductance *versus* 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 is shown in (Fig. 3). The resulting K_β of the $PYTANO_2$ complexes at 25 °C are listed in (Table-1).
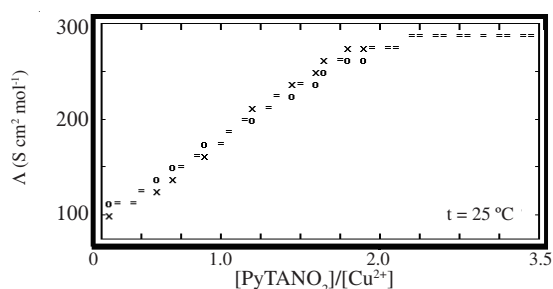

Fig. 3.   Computer fit of molar conductance *versus* [PYTANO₂]/[Cu²⁺] mole ratio plot in acetonitrile at 25 °C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

All of the log K_β 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_β *versus* 1/T, for metals complexes in acetonitrile were linear and are shows in Fig. 4.
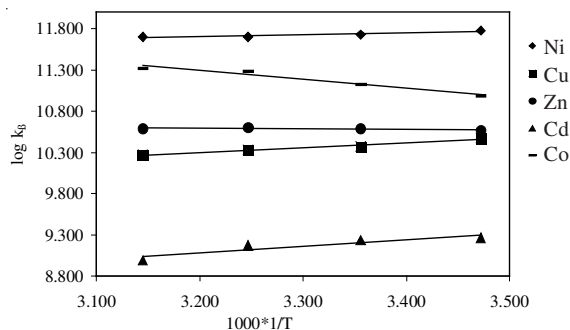

Fig. 4. log K_β *versus* 1/T for metal ions complexes with PYTANO₂

TABLE-1

FORMATION CONSTANT VALUES AND THERMODYNAMIC PARAMETERS FOR
$M(PYTANO_2)_2$ COMPLEXES AT DIFFERENT TEMPERATURES

Metal	15 ºC	25 ºC	35 ºC	45 ºC
	$\log k_\beta \pm SD$			
Co^{2+}	10.99 ± 0.01	11.13 ± 0.01	11.29 ± 0.03	11.32 ± 0.01
Ni^{2+}	11.78 ± 0.01	11.73 ± 0.02	11.70 ± 0.02	11.70 ± 0.01
Cu^{2+}	10.47 ± 0.01	10.37 ± 0.02	10.33 ± 0.02	10.27 ± 0.01
Zn^{2+}	10.57 ± 0.02	10.59 ± 0.01	10.60 ± 0.02	10.59 ± 0.01
Cd^{2+}	9.26 ± 0.01	9.23 ± 0.02	9.17 ± 0.01	8.99 ± 0.02

Metal	Complex	
	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} k^{-1})
Co^{2+}	20.28	281.14
Ni^{2+}	-4.79	208.72
Cu^{2+}	-11.26	161.14
Zn^{2+}	1.26	206.88
Cd^{2+}	-15.07	125.62

SD = standard deviation.

ΔH° and ΔS° values were determined from Van't Hoff eqn. 1 in the usual manner from the slopes and intercepts of the plots, respectively and the results are presented in Table-3. Comparison of the data given in Table-1 indicate that the stability of the complexes to vary in the order $Ni^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$.

The thermodynamic data in Table-1 reveal that the enthalpy for formation of complexes for Co, Zn, is positive. It means that formation of this complexes is enthalpy desirable and in all cases the complexes are entropy stabilized.

In conductometric method, the addition of ligand to metal cations causes the formation of the ML complexes due to presence of less amount of ligand in the first and then the formation of ML_2 complexes in higher ligand to metal cation mole ratios. The ML_2 complexes are superior to ML complexes and therefore, the mole ratio plots indicate weak curvature in 1:1 and strong curvature in 2:1 ligand to metal cation mole ratios (Fig. 2).

REFERENCES

1. H. Schiff, *Ann. Suppl.*, **3**, 343 (1864).
2. D.A. Atwood and M.J. Harvey, *Chem. Rev*., **101**, 37 (2001).
3. R.H. Holm, G.W. Evertett and A.P. Chakravory, *Inorg. Chem.*, **7**, 83 (1966).
4. A.D. Granovskii, A.L. Nivorozhkin and V.I. Minkin, *Coord. Chem. Rev*., **126**, 1 (1993).
5. E.N. Jacobson, W. Zhang, A.R. Muci, J.R. Ecker and L.I. Deng, *J. Am. Chem. Soc*., **113**, 7063 (1991).
6. A. Giacomelli, T. Rotunno and L. Senatore, *Inorg. Chem.*, **24**, 1303 (1985).
7. L. Carbonaro, M. Isola, P. L. Pegna and L. Senatore, *Inog. Chem.*, **38**, 5519 (1999).
8. N. Alizadeh, S. Ershad, H. Naeimi, H. Sharghi and M. Shamsipur, *Polish J. Chem.*, **73**, 915 (1999).
9. B. Rihter, S. Srihari, S. Hunter, J. Masnovi and J. Masnovi, *J. Am. Chem. Soc*., **115**, 3918 (1993).

10. W. Zhang, J.L. Loebach, S.R. Wilson and E.N. Jacobsen, *J. Am. Chem. Soc.*, **112**, 2801 (1990).
11. Z. Li, K.R. Conser and E.N. Jacobsen, *J. Am. Chem. Soc.*, **115**, 5326 (1993).
12. M. Aurangzeb, C.E. Hulme, C.A. McAuliffe, R.G. Richard, A. Watkinson Garica-Deibe, M.R. Bermjo and A. Sousa, *J. Chem. Soc. Chem. Commun.*, **41**, 1524 (1992).
13. M. Shamsipur, M. Yousefi, M. Hossein, M.R. Ganjali, H. Sharghi and H. Naeimi, *Anal. Chem.*, **73**, 2869 (2001).
14. N. Daneshvar, A.A. Entezami, A.A. Khandar and L.A. Saghatforoush, *Polyhedron*, **22**, 1437 (2003).
15. V.A. Nicely and J.L. Dye, *J. Chem. Educ.*, **49**, 443 (1971).
16. M. Shamsipur, A. Avanes, G. Aghapour and H. Sharghi, *Polish J. Chem.*, **75**, 1533 (2001).
17. H. Strehlow and H.M. Koepp, *Electrochemistry*, **62**, 373 (1958).
18. D. Marji and Z. Taha, *J. Incl. Phenom.*, **30**, 309 (1998).