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# CONDUCTOMETRIC STUDY OF COMPLEX FORMATION BETWEEN 2,3-PYRAZINEDICARBOXYLIC ACID AND SOME TRANSITION METAL IONS IN METHANOL



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**ABSTRACT**

*The complexation reactions between $CuCl_2$, $CoCl_2$ and $NiCl_2$ with 2,3-Pyrazinedicarboxylic acid in methanol (MeOH) at 313.15 K were studied by conductometric methods. The association constants, formation constants and Gibbs free energies were calculated from the conductometric titration curves. On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines were obtained indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants and Gibbs free energies of different complexes in absolute Methanol at 313.15 K follow the order:)*

*$K_f(2:1)>K_f(1:1)$for (M:L) and $\triangle G_f(2:1)>\triangle Gf(1:1)$ for (M:L)*

**KEY WORDS:** Association constants; formation constants; Gibbs free energies of association; Gibbs free energies of complex formation.

**RESUMO**

*A formação de complexos entre $CuCl_2$, $CoCl_2$ , $NiCl_2$ e ácido 2,3-pirazinodicarboxílico em metanol á 313.15 K foi estudada usando métodos de condutividade. As constantes de associação e formação e as energias livres de Gibbs foram calculadas a partir de curvas de titulação condutimétrica. A relação entre a condutância molar e a proporção das concentrações metal-ligante levou a linhas retas indicando a formação de complexos estequiométricos (M:L) 1:1 e 2:1. As constantes de formação e as energias livres de Gibbs dos vários complexos em metanol à 313.15 K seguem a ordem:*

*$K_f(2:l)>K_f(1:1)$ para (M:L) e $\triangle Gf(2:1)>\triangle G_f(1:1)$ para (M:L)*

**PALAVRAS CHAVE:**Constantes de associação. Constantes de formação,Energias livres de Gibbs de associação, energias livres de Gibbs para formação de complexos.

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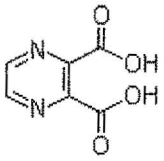
## INTRODUCTION

The long range ion – ion interactions due to screened columbic forces are the most important features of electrolyte in solutions. These act together with shorter – ranged forces between the solvent molecules and between the solvent molecules and ion. Electrical conductivity (EC) is a measure measure of solvent to conduct electric current and depends on: concentration of the ions, ligand and temperature in solutions. Current is carried out by both cations and anions, but to different degree. The conductivity due to divalent cations is more than that of mono-valet cations, it is not true for anions. Metal cations with $d^0$ noble gas electron configuration (alkali and alkaline earth) metal ions together with the inert molecular ions like tetraalkylammonium,-phosphonium,-arsonium , and trialkylsulfonium ions exhibit properties mainly determined by their charge and size [1].Solvation of such cations in protic and polar solvents is due essentially to electrostatic ion-dipole and ion induced dipole interactions. Metal cations with filled d - orbitals, the $d^{10}$ cations, exhibit partially covalent character in their interactions; their properties depend on the charge and size and partially on their electro negativity. Cations with incomplete d- orbitals called $d^n$-cations .With these cations protic and polar solvent molecules are strongly bound in complexes to a central cation through p-d orbital overlap and exchange only slowly with the bulk solvent. The formation of complexes becomes more important at high concentration of the complex ion and is likely to be more extensive in non-aqueous solvents, particularly in dipolar aprotic solvents, whereas the salvation of anions is weaker, leading to stronger complexation. Therefore conductivity study is valuable on using transition metal cations [2-7]. This work provides the analytical analyst and the biological analyst data can help him for deterring the concentration of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in blood and different solutions.

2,3-Pyrazinedicarboxylic acid

Identification

| | |
|---|---|
| Name | 2,3-Pyrazinedicarboxylic acid |
| Synonyms | Pyrazine-2,3-dicarboxylic acid |
| Molecular Structure |  |
| Molecular Formula | $C_6H_4N_2O_4$ |
| Molecular Weight | 168.11 |
| CAS Registry Number | 89-01-0 |
| EINECS | 201-875-3 |

Properties

| | |
|---|---|
| Melting point | 185-188 °C |
| Water solubility | Soluble |

## EXPERIMENTAL

The chemicals used 2, 3-pyrazine dicarboxylic acid and methanol were provided from Merck Co. and used directly without purification.

The experimental procedure to obtain the formation constant of complexes of 2,3-Pyrazinedicarboxylic acid with $CuCl_2$, $CoCl_2$ and $NiCl_2$ by conductometric procedure was as follows : -

A solution of metal chloride ($1x10^{-3}$ M) was placed in a titration cell, at a const temperature (313.15) K , and the conductance of the solution was measured . The ligand ($1\times10^{-2}$ M) was transferred step-by-step to the titration cell using a precalibrated micropipette and the conductance of the solution was measured after each transfer. Addition of the ligand solution was continued until the total concentration of the (2, 3-Pyrazinedicarboxylic acid) was approximately four times higher than that of metal ions. The conductance of the solution was measured after each addition. The complex formation constant, $K_f$, and the molar conductance of the complex, ML, were evaluated by computer fitting to the molar conductance mole ratio data.

## RESULTS AND DISCUSSIOIN

- The stability of a transition metal complex with a polydentate chelate ligand depends on a range of factors including: number and type of the donor atoms present, the number and size of the chelate rings formed on complexation. In addition, the stability and selectivity of complexities strongly depend on the donor ability and dielectric constant of the solvent and shape and size of the solvent molecules.

- 2, 3-Pyrazinedicarboxylic acid is a polydentate ligand which tends to be completely coordinated to a metal ion. This reagent is soluble in water and soluble in most organic solvents

- The specific conductance values (Ks) of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in absolute (MeOH) were measured experimentally in absence and in the presence of ligand at 313.15 K.

The molar conductance ($\Lambda_m$) values were calculated [8] using equation (1):

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \quad (1)$$

Where $K_s$ and $K_{solv}$ are the specific conductance of the solution and the solvent, respectively; $K_{cell}$ is the cell constant and C is the molar concentration of the $CuCl_2$, $CoCl_2$ and $NiCl_2$ solutions.

- The limiting molar conductances ($\Lambda_o$) at infinite dilutions were estimated $CuCl_2$, $CoCl_2$ and $NiCl_2$ in absolute methanol (MeOH) alone and in the presence of the ligand by extrapolating the relation between $\Lambda_m$ and $C_m^{1/2}$ to zero concentration (Fig.1). By drawing the relation between molar conductance ($\Lambda_m$) and the molar ratio of metal to ligand (M/L) concentrations , different lines are obtained with sharp breaks indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes (Fig.2).

- The experimental data of ($\Lambda_m$) and ($\Lambda_o$) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes.

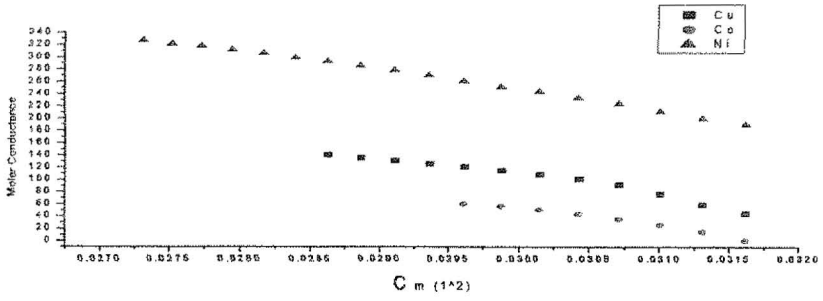



Figure 1. The relation between molar conductance ($\Lambda_m$) and ($\sqrt{C}$) of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of $H_2L$ in absolute methanol at 313.15 K.

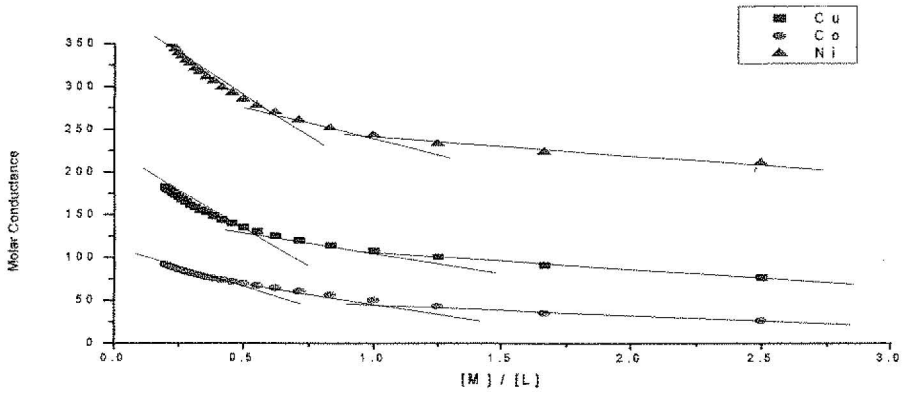



Figure 2. The relation between molar conductance ($\Lambda_M$) and the molar ratio (M/L) of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of $H_2L$ in absolute methanol at 313.15 K indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes.

- The association constants of $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of ligand in absolute MeOH at 313.15 K for 1:2 asymmetric electrolytes were calculated [9, 10] by using equation (2):

$$K_A = \frac{\Lambda_0^2(\Lambda_0 - \Lambda_m)}{4C_m^2 + \Lambda^3 S(z)} \qquad (2)$$

Where ($\Lambda_m$, $\Lambda_0$) are the molar and limiting molar conductance, respectively of $CuCl_2$, $CoCl_2$ and $NiCl_2$ , $C_m$ is molar concentration of $CuCl_2$, $CoCl_2$ and $NiCl_2$ , S(Z) is Fuoss-Shedlovsky factor , equal one for strong electrolytes [11]. The calculated association constants are shown in Table 1.

- The Gibbs free energies of association ($\Delta G_A$) were calculated from the association constant [12,13] by applying equation (3) :

$$\Delta G_A = -R\,T \ln K_A \qquad (3)$$

Where R is the gas constant (8.341 J) and T is the absolute temperature (313.15 K). The calculated Gibbs free energies were presented in Table 1.

Table 1. Association constants and Gibbs free energies of association for $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the presence of ligand in absolute MeOH at 313.15 K .

| C | $\Lambda_m$ | | | $\Lambda_0^2$ ($\Lambda_0$-$\Lambda_m$) | | | $4C^2+\Lambda^3_m$ | | | $K_A$ | | | $\Delta G_A$ (k J/mol) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni |
| 0.001 | 44.2365 | 1.5347 | 190.1071 | 4153605 | 409822.3 | 35726553 | 7828.18 | 3.614689 | 6870605 | 530.622 | 113404.6 | 5.199913 | -16.3877 | -30.4001 | -4.30623 |
| 0.00098 | 58.78107 | 14.99206 | 199.8977 | 3698561 | 334627.6 | 34109455 | 13820.86 | 3369.845 | 7987726 | 267.6072 | 99.30655 | 4.270234 | -14.5997 | -12.0105 | -3.78174 |
| 0.000962 | 76.43012 | 26.64074 | 211.637 | 3146071 | 269453 | 32170481 | 23366.25 | 16907.72 | 9479266 | 134.6416 | 14.25095 | 3.393774 | -12.8056 | -6.93958 | -3.19169 |
| 0.000943 | 91.21989 | 35.77829 | 224.4413 | 2683089 | 218328.1 | 30055600 | 33264.27 | 45799.27 | 11305987 | 80.6113 | 4.767064 | 2.658379 | -11.4657 | -4.07922 | -2.55378 |
| 0.000926 | 100.9503 | 43.57271 | 234.2381 | 2378486 | 174717.9 | 28437481 | 40763.85 | 82726.31 | 12852051 | 58.34791 | 2.112 | 2.21268 | -10.6214 | -1.95281 | -2.07445 |

- The association free energies evaluated for CuCl2, CoCl2 and NiCl2 -ligand complexes are small and spontaneous indicating electrostatic attraction.
- The formation constants ($K_f$) for $CuCl_2$, $CoCl_2$ and $NiCl_2$ complexes were calculated for each type of complexes (1:1) and (2:1) (M:L) by using equation (4) [14,15] :

$$K_f = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (4)$$

Where $\Lambda_m$ is the molar conductance of the CuCl2, CoCl2 and NiCl2 alone, $\Lambda_{obs}$ is the molar conductance of solution during titration and $\Lambda_{ML}$ is the molar conductance of the complex.

- The obtained values ($K_f$) for $CuCl_2$, $CoCl_2$ and $NiCl_2$ -ligand stoichiometric complexes are presented in Table 2, 3. The Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation :

$$\Delta G_f = -R\ T \ln K_f \qquad (5)$$

- The calculated $\Delta G_f$ values are presented in Tables 2, 3.

Table 2. Formation constants and Gibbs free energies of formation for 1: 1 (M/L) , $CuCl_2$, $CoCl_2$ and $NiCl_2$-$H_2L$ in absolute MeOH at 313.15 K .

| [L] | $\Lambda_{obs}$ | | | $(\Lambda_{obs}-\Lambda_{ML})/[L]$ | | | $(\Lambda_m-\Lambda_{obs})$ | | | $K_f$ | | | $\Delta G_f$ (k J/mol) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni |
| 0.001525 | 130.5947 | 70.41492 | 279.0194 | 0.03436 | 0.026712 | 0.054091 | 381.4053 | 422.3387 | 170.9806 | 11100.35 | 15810.72 | 3161.006 | -24.3299 | -25.2538 | -21.0491 |
| 0.001379 | 125.2748 | 67.66132 | 270.7058 | 0.023731 | 0.020429 | 0.037443 | 386.7252 | 425.0387 | 179.2942 | 16296.39 | 20805.3 | 4788.516 | -25.3328 | -25.9709 | -22.1339 |
| 0.001228 | 120.062 | 64.96128 | 261.3417 | 0.014727 | 0.013209 | 0.021837 | 391.9381 | 429.0942 | 188.6583 | 26613.65 | 32485.43 | 8639.321 | -26.514 | -27.1347 | -23.6752 |
| 0.001071 | 114.3794 | 60.90575 | 252.1424 | 0.00676 | 0.007413 | 0.009195 | 397.6206 | 432.9314 | 197.8576 | 58818.62 | 58403.4 | 21517.08 | -28.6654 | -28.6669 | -26.0587 |
| 0.000909 | 108.2582 | 57.08869 | 244.2408 | 0.000171 | 0.000831 | 0.000619 | 403.7419 | 438.9357 | 205.7592 | 2360436 | 528080.5 | 332449.7 | -36.3292 | -34.4181 | -33.2094 |

Table 3. Formation constants and Gibbs free energies of formation for 2:1 (M/L) $CuCl_2$, $CoCl_2$ and $NiCl_2$-$H_2L$ in absolute MeOH at 313.15 K.

| [L] | $\Lambda_{obs}$ | | | $(\Lambda_{obs}-\Lambda_{ML})/[L]$ | | | $(\Lambda_M-\Lambda_{obs})$ | | | $K_f$ | | | $\Delta G_f$ (k J/mol) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni | Cu | Co | Ni |
| 0.002186 | 153.0003 | 77.87709 | 311.6939 | 0.03931 | 0.016292 | 0.05883 | 359.9997 | 412.1221 | 136.1061 | 9132.511 | 26295.58 | 2347.531 | -23.8202 | -26.4813 | -20.2719 |
| 0.002063 | 148.7928 | 76.53127 | 307.0205 | 0.028399 | 0.01259 | 0.045439 | 363.2072 | 413.4687 | 142.9795 | 12789.27 | 32841.27 | 3146.609 | -24.6999 | -27.1632 | -21.0371 |
| 0.001935 | 144.3875 | 74.42244 | 299.5928 | 0.018111 | 0.007727 | 0.028044 | 367.6125 | 415.5776 | 150.4072 | 20297.51 | 53760.36 | 5325.254 | -25.9063 | -28.4515 | -22.4114 |
| 0.001803 | 140.1737 | 72.46812 | 293.5041 | 0.009276 | 0.003675 | 0.015335 | 371.8263 | 417.5319 | 156.4959 | 40066.58 | 113604.8 | 10205.02 | -27.6839 | -30.4048 | -24.1103 |
| 0.001667 | 135.4038 | | 286.2205 | 0.000623 | | 0.002034 | 376.5962 | | 163.7795 | 504488.3 | | 80512.97 | -34.7711 | | -29.5054 |

- The association free energies evaluated for CuCl2, CoCl2 and NiCl2 -1igand complexes indicating a spontaneous electrostatic attraction.

- The formation constants and Gibbs free energies of different complexes in absolute methanol at 313.15 K follow the order: $K_f$ (2:1) › $K_f$ (1:1) for (M:L), and $\Delta G_f$(2:1) › $\Delta G_f$(1:1) for (M:L) .

## CONCLUSION

This work concentrated on the behavior of $CuCl_2$, $CoCl_2$ and $NiCl_2$ with the ligand conductometrically .The main target is to discuss the complexation between the metal and ligand for evaluating different concentrations from the metal ion in different solutions

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