Thermodynamic Studies on Electron Donor - Acceptor Interaction of Nano Cobalt Sulphate with 4-imino-1-phenyl -3(p-tolyl) -1,4 dihydro-5H-pyrazolo [3,4-d] pyrimidin-5-amine in Mixed N,N-Dimethyl - formamide – Water Solvents

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Citation

Abstract
The complex formation constant for the interaction of any salt with ligand gave important data about the interaction between them. Special interest in applications is the comparison between the behaviors in using bulk (normal) and nano salts. Using nano salts, very fine grains in the nanometer form improve the physical properties of the used salts that can be used in many areas in industry like pharmaceutical and medical branch. Cobalt salts is the main source for B-complex drugs can help us in improving the branch of Vitamins in Medical factories by increasing its physical properties. Using new ligand as shown here introduce to the pharmaceutical science new reagent can help in the using of cobalt salts in manufacturing and application in paints as its color is red and also application in battery factor because its strong electrolyte can easily be applied Condutometric method is easily used, cheap and fast method for following the behaviors of bulk and nano salts in different solvents and solutions.. Among the condutometric models used in thermodynamic parameters evaluation we used Debye-Hückel limiting law to be followed here in this to give results for further discussions. Using new ligand (complexion agent) which is novel in study to follow the solution behaviors for nano cobalt sulphate is interesting and valuable results which many scientists search for them .Stability constants or complex formation constants (Kf) are measured for complexes of nanometric ions of Co^{2+} with 4-imino-1-phenyl-3(p-tolyl)-1,4 dihydro-5H-pyrazolo[3,4-d]pyrimidin-5-amine (IPPA) by applying the condutometric method. The selectivity between ligand and ions in various systems and thermodynamic parameters of complexation is very interesting to have complete pictures about the behavior of salts in solution. On drawing the relation between molar conductance and the ratio of metal to the ligand concentrations, different lines are obtained indicating the formation of 1:2 and 1:1 (M:L) stoichiometry complexes. The ΔH and ΔS° of the complexation reaction in the different H2O -DMF binary mixtures were evaluated by the temperature dependence of the formation constants using a linear least square analysis according to Van’T Hoff equation. The data given here in this work can help for the analytical determination of cobalt ions generally and especially nano cobalt...
salts in human body environment and coloring materials in food industry.

1. Introduction

Metal complex study is well established area of research works. To study the formation constants of ligand with metal ions in solution conductometrically using conductivity method is widely used because of its various advantages such as low cost, eco-friendly, less time consuming, proper thermodynamic calculation with different parameters and most important easy to operate. Using conductometric method, researcher can calculate all thermodynamic parameters for specific reactions and also investigate stability constant. By using conductometric method, basic research on thermodynamic studies like enthalpy, entropy, Gibbs free energy can also be determined. The factors responsible for the stability of complexes are charge and size of the metal ion, type of the metal ion, counter ion nature of the ligand temperature and physical properties of solvents. From conductometric method, the stability constant or the complex formation constant (\(\log K_f\)) can be evaluated by GENPLOT computer program. The enthalpy change (\(\Delta H\)) and entropy change (\(\Delta S\)) of the complexation reactions in the different binary mixtures can be calculated by temperature dependence of the formation constant using a linear least square analysis according to Van’t Hoff equation. We use the salt in nano size because nano particles are incredibly essential for medicine in addition to environment, because of their increased behaviors due to their high surface area and small volume makes them very reactive.

2. Materials and Methods

2.1. Materials

All glass wares used are from Pyrex ‘A’ grade quality. Cobalt sulfate heptahydrate (\(\text{CoSO}_4 \cdot 7\text{H}_2\text{O}, \text{E. Merck, 99 % pure}\), and DMF of E. Merck (HPLC grade) were used without further purification. Deionized water was used for preparation of different percentages (10 % to 50 %v/v) of aqueous DMF systems. Digital direct reading conductivity meter model HI-9813, Hanna used to measure the conductivities, having a conductivity electrode with cell constant equal 1.

Synthesis of 4-imino-1-phenyl-3-(p-tolyl)-4,4-dihydro-5H-pyrazolo[3,4-d]pyrimidin-5-amine: The novel compound 4-imino-1-phenyl-3(p-tolyl)-4,4-dihydro-5H-pyrazolo[3,4-d]pyrimidin-5-amine was prepared as shown in Scheme 1. Hydrazonoyl chloride 1 was treated with malononitrile in the presence of sodium ethoxide solution at room temperature to give 4-cyano-5-aminopyrazole 2. Treatment of 2 with triethyloorthoformate in boiling dioxane afforded ethoxymethylene derivative 3. The latter compound 3 was stirred with hydrazine hydrate in ethanol for 6 h the solid was collected and crystallized from dioxane to give the target compound 4. The structures of the products 2, 3 and 4 were established on the basis of (\(^1\)H NMR, \(^{13}\)C NMR, IR, and Ms) spectra in addition to elemental analysis.

\[
\begin{align*}
\text{Cl} & \quad \text{Ph} & \quad \text{N} & \quad \text{H} & \quad \text{N} & \quad \text{Ph} \\
1 & \quad + & \quad \text{CH}_2(\text{CN})_2 & \quad \xrightarrow{\text{NaOEt, EtOH}} & \quad \text{EtO} & \quad \text{CH} \\
2 & \quad \xrightarrow{\text{NH}_{2}\text{NH}_2, \text{EtOH}} & \quad \text{3} \\
3 & \quad \xrightarrow{\text{R=H}_2\text{C}-\text{Ph}} & \quad \text{4} \\
\text{Scheme 1} & \quad \text{Reaction steps for preparation of for 4-imino-1-phenyl-3(p-tolyl)-4,4-dihydro-5H-pyrazolo[3,4-d]pyrimidin-5-amine.}
\end{align*}
\]
2.2. Preparation of Nano Cobalt Sulphate

Nano CoSO₄ was prepared by shaking bulk CoSO₄ in ball–mill apparatus. The ball–mill was a Retsch MM2000 swing mill with 10 cm³ stainless steel, double–walled tube. Two stainless steel balls of 12 mm diameter and 7 gm weight for each were used. Ball-milling was performed at 20225 Hz for half an hour at room temperature.

3. Measurement of Conductance and Evaluation of Stability Constant (Kᵢ)

The change in conductance is measured when a metal salt solution to which ligand solution is added, this provides valuable information about metal ligand interactions. Conductance measurement gives information about the affinity of the ligand and the stoichiometry of the complexation reaction. The measurement of conductance is carried out as the following. In a typical experiment, 5 ml of CoSO₄.7H₂O solution (1.0 x 10⁻³ M) was placed in the titration cell, thermostated at the preset temperature and the conductance of the solution was measured after the solution reached thermal equilibrium. Then, a known amount of the ligand solution (1.0 x 10⁻³ M) was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition until the desired concentration to-ligand mole ratio was achieved. The specific conductance values were recorded. The conducto meter was conducted with a thermostat of the type the Kottermann 4130 ultra-thermostat. There are two factors responsible for very small change in conductance in spite of an increase in the concentration of ligand, firstly when there is no complexation occurs between metal ion and ligand and secondly mobilities of a resulting metal-ligand complex and the corresponding metal ions are both equal at the same concentration. The first factor is responsible in the most of the cases. When the dielectric constant of the solvent is very high and conductance measurements are made at low concentration, the correction for viscosity changes and association between the metal ion, uncomplexed metal ion, an ion and the ligand metal complex are neglected. The stability constant can be described for a 1:1 metal-ligand binding is as follows:

\[
\text{M}^{++} + \text{L} = \text{ML}^{+}
\]  

Where, M⁺⁺, L and ML⁺ represent the free solvated cation, the free ligand, and the complex, respectively. The thermodynamic equilibrium constant \(K_f\) for the association is given by

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

Where, \([\text{ML}^{+}]\), \([\text{M}^{n+}]\), \([\text{L}]\) and \(f\) represent the equilibrium molar concentration of the complex, the free cation, the free ligand and the activity coefficients of the species indicated respectively. Under the dilute, where the ionic strength is less than 0.001M, the activity coefficient of the uncharged ligand \(f(\text{L})\) can be reasonably assumed to be unity. The use of the Debye - Hückel limiting law of electrolytes leads to the conclusion that \(f(\text{ML}^{+}) \approx \bar{f}(\text{M}^{+})\); thus, equation²⁻¹⁸ reduces to

\[
K_f = \frac{[\text{ML}^{+}]\bar{f}(\text{ML})^{n+}}{[\text{M}^{n+}]\bar{f}(\text{L})\text{[L]}(\text{ML})^{n+}\bar{f}(\text{L})}
\]  

If \(\alpha\) is the fraction of total metal cation that is uncomplexed with the ligand, then the following equations result:

\[
[M^+] = \alpha [M]^t
\]  

\[
[ML^+] = (1 - \alpha)[M]^t
\]  

\[
[L] = [L]^t (1 - \alpha)[M]^t
\]  

Where \([M]^t\), \([M^+]\), \([ML^+]\) and \([L]\) represent the concentration (in molarities) of total cation total ligand, free uncomplexed cation, and the complex and free solvated ligand respectively. The dilute conditions used make it possible to neglect ion aggregation and corrections for viscosity changes. The molar conductivities \(\Lambda\) can be calculated by using the following

\[
\Lambda = \frac{1000 K}{[M]^t}
\]  

Where \(k\) is the conductivity of the used solutions in Siemens.cm⁻¹. On the other hand, \(\Lambda\) can be related to \(\alpha\) by the following equation,

\[
\Lambda = \alpha \Lambda_{ML^+} (1 - \alpha)\Lambda_{ML}
\]  

Where, \(\Lambda_{ML}\) and \(\Lambda_{ML^+}\) represent the molar conductivities of the ligand free metal salt solution and the complexed cation solution at the same concentration, respectively.

Rearranging Equation 7.3 gives an expression for \(\alpha\) as;

\[
\alpha = \frac{\Lambda - \Lambda_{ML}}{\Lambda_{ML^+} - \Lambda_{ML}}
\]  


\[
K_{ML^+} = (1 - \alpha)/\alpha [L]
\]  

Substituting the value of \(\alpha\) from equation [9] in [10]⁹⁻⁻³⁰:

\[
K_{ML^+} = \frac{\Lambda_{ML^+}t - \Lambda}{\Lambda - \Lambda_{ML}t} [M]^t
\]  


\[
K_{ML} = \frac{\Lambda_{ML}t - \Lambda}{\Lambda - \Lambda_{ML}t} [M]^t
\]  

Substitution of equation [12] into equation [11] gives the expression⁵⁻⁻⁶⁰ for \(K_{ML^+}\)

\[
K_{ML^+} = \frac{\Lambda_{ML^+}t - \Lambda}{\Lambda - \Lambda_{ML}t} [M]^t
\]
4. Results and Discussion

TEM Imagies

All images measured by using JEOL HRTEM – JEM 2100(JAPAN) show that TEM of CoSO$_4$ obtained in methanol are irregular spheres in the form of cylinders Fig. 1. The diameter in the range of 1 - 30 nm. The small sizes in the range between 1, 11 are collected to give bigger sizes till 30 nm. The non homogeneity in sizes for nano cobalt sulfate need controlling during the primary preparation of the samples.

In all cases studied, addition of the CoSO$_4$.7H$_2$O solution to the ligand (IPPA) solutions caused a continuous decrease in the molar conductance of the solutions, indicating the lower mobility of the complexed cation compared to the solvated ones. In all cases, the slope of the molar conductance-mole ratio plots change sharply at the point where the ligand to cation mole ratio is one, indicating the formation of a relatively stable 1:2, 1:1 [M : L] complex between the ligand and the cation solutions used, see Fig.2-5. For enthalpy and entropies calculation the relations between log K$_f$ and 1/T were done in the range from 10% to 50% DMF as given in Fig.6-10.

![Fig. 1. TEM images for nano cobalt sulphate (a) and (b) where (c) is electron diffraction image.](image1)

![Fig. 2. The relation between molar conductance ($\Lambda_m$) and the [M]/[L] molar ratio of nano CoSO$_4$.7H$_2$O to IPPA in different aqueous - DMF solvents at 298.15 K.](image2)

![Fig. 3. The relation between molar conductance ($\Lambda_m$) and the [M]/[L] molar ratio of nano CoSO$_4$.7H$_2$O to IPPA in different aqueous - DMF solvents at 303.15 K.](image3)

![Fig. 4. The relation between molar conductance ($\Lambda_m$) and the [M]/[L] molar ratio of nano CoSO$_4$.7H$_2$O to IPPA in different aqueous DMF solvents at 308.15 K.](image4)
Fig. 5. The relation between molar conductance ($\Lambda_m$) and the [M]/[L] molar ratio of nano CoSO$_4$·7H$_2$O to IPPA in different aqueous - DMF solvents at 313.15 K.

Fig. 6. The relation between log $K_f$ for (1:2) and (1:1) stoichiometric complexes between nano CoSO$_4$·7H$_2$O and IPPA against 1/T in 10% DMF-water.

Fig. 7. The relation between log $K_f$ for (1:2) and (1:1) stoichiometric complexes between nano CoSO$_4$·7H$_2$O and IPPA against 1/T in 20% DMF-water.

Fig. 8. The relation between log $K_f$ for (1:2) and (1:1) stoichiometric complexes between nano CoSO$_4$·7H$_2$O and IPPA against 1/T in 30% DMF-water.

Fig. 9. The relation between log $K_f$ for (1:2) and (1:1) stoichiometric complexes between nano CoSO$_4$·7H$_2$O and IPPA against 1/T in 40% DMF-water.

Fig. 10. The relation between log $K_f$ for (1:2) and (1:1) stoichiometric complexes between nano CoSO$_4$·7H$_2$O and IPPA against 1/T in 50% DMF-water.
Table 1. The formation constants (log $K_f$) of formation of nano CoSO$_4$.7H$_2$O and IPP A complexes in mixed DMF-water at different temperatures.

<table>
<thead>
<tr>
<th>Vol.% of DMF</th>
<th>log $K_f$</th>
<th>1:2 M:L</th>
<th>1:1 M:L</th>
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<tbody>
<tr>
<td></td>
<td>298.15</td>
<td>303.15</td>
<td>308.15</td>
</tr>
<tr>
<td>40</td>
<td>3.2596</td>
<td>3.1089</td>
<td>3.0235</td>
</tr>
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Table 2. The Gibbs free energies ($\Delta G_f$) of nano CoSO$_4$.7H$_2$O and IPP A complexes in DMF-water at different temperatures.

<table>
<thead>
<tr>
<th>Vol.% of DMF</th>
<th>($\Delta G_f$)</th>
<th>kJ mol$^{-1}$</th>
<th>1:2 M:L</th>
<th>1:1 M:L</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
<th>313.15</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
<th>313.15</th>
</tr>
</thead>
</table>

Table 3. The enthalpies ($\Delta H_f$) in (kJ mol$^{-1}$) and entropies ($\Delta S_f$) in (J mol$^{-1}$K$^{-1}$) of formation of nano CoSO$_4$.7H$_2$O and IPP A complexes in DMF-water at different temperatures.

<table>
<thead>
<tr>
<th>Vol.% of DMF</th>
<th>($\Delta H_f$)</th>
<th>(kJ mol$^{-1}$)</th>
<th>1:2 M:L</th>
<th>1:1 M:L</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
<th>313.15</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
<th>313.15</th>
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<tbody>
<tr>
<td>10</td>
<td>37.775</td>
<td>37.2591</td>
<td>38.019</td>
<td>37.522</td>
<td>95.2898</td>
<td>96.1428</td>
<td>95.033</td>
<td>95.656</td>
<td></td>
<td></td>
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<tr>
<td>20</td>
<td>42.544</td>
<td>41.6281</td>
<td>42.089</td>
<td>42.403</td>
<td>115.2206</td>
<td>116.576</td>
<td>115.52</td>
<td>115.55</td>
<td></td>
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<tr>
<td>30</td>
<td>66.480</td>
<td>62.1840</td>
<td>65.605</td>
<td>65.385</td>
<td>122.3853</td>
<td>124.453</td>
<td>122.69</td>
<td>122.95</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>50</td>
<td>34.285</td>
<td>34.15076</td>
<td>34.375</td>
<td>34.209</td>
<td>119.3327</td>
<td>119.454</td>
<td>119.45</td>
<td>119.04</td>
<td></td>
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Scheme 2. Structure of 4-imino-1-phenyl-3(p-tolyl)-1,4 dihydro-5H-pyrazolo [3,4-d]pyrimidin-5-amine in 3D and 2D directions:
5. Conclusion

Studying the complex behavior between the metal ion in nano form and new ligand give new data which is vakuablre in following the concentration of this metal salt in environment. Also this study can be used as new analytical method for the determination of small amounts of cobalt ion in different solutions by direct and fast method . The engineers and scientists using cobalt salts can use these new data given in this work for nano cobalt sulphate in solutions for different manufacturing in batteries, paints and drugs.

According to the results obtained in the present work, complexes formed between the ligand and the metal cation, it indicates the probability of changes in the stabilities and stoichiometry of the complexes due to the composition of the solvent systems. IPPA formed 1:2 and 1:1 complexes with Co^{2+}. The results obtained in our studies suggest that stability of the complexes of IPPA with the metal cation in solutions undergoes the chemical and physical properties of each solvent molecule such as donor number and polarity and with increasing DMF percent when mixed one another and therefore changing their solvating ability towards the ligand, metal cation and the resulting complex .The negative values of ΔG shows the ability of the studied ligand to form stable complexes and process trends to be spontaneously. In 1:2 complexes the obtained positive value of ΔH indicates that the enthalpy is not driving force for the formation of the complexes and the formation of the complexes is exothermic reactions but formation complex 1:1 is endothermic reaction. Furthermore, the positive value of ΔS indicates that entropy is a driving force for the complexation reaction. Using new ligand, complexion agent (IBPA) which is novel in study to follow the solution behaviors for nano cobalt sulphate is interesting and valuable results which many scientists search for them. The data given here in this work can help for the analytical determination of cobalt ions generally and especially nano cobalt salts with low concentrations in human body, environment and coloring materials in food industry.

References


