Electron Donor-Acceptor Interaction Parameters of Calcon Carboxylic Acid with Nano Cobalt Sulphate in Methanol ( Meoh ) - Water at Different Temperatures by Applying Conductance Studies

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Abstract
Nanoparticles 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. This article summarizes different aspects of the complexes of the nano CoSO₄ with ligand Calcon carboxylic acid (Calcon CA) as studied conductometrically in mixed methanol-water solvent at 298.15, 303.15, 308.15 and 313.15K by applying the conductometric method. Consequently, we will study the effect of solvent properties, (MeOH/H₂O) on stoichiometry, the selectivity between ligand and ions in various systems and thermodynamic parameters of complexation. On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines are obtained indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometry complexes.

Keywords: Nanoparticles, Thermodynamic Parameters, Calcon CA, MeOH-H₂O, Conductance, Nano Cobalt Sulphate, Complex Formation.

1. Introduction
Conductance research of electrolytes in mixed solvents has received considerable interest in recently. It is a simple method to study the solvents effects, nature of ion, ion-solvent interaction existing in the system, modification in the structure of a solvent because of the presence of an ion and ionic movement in a solution. The study of variation in molar conductance with temperature and solvent composition provides information about ionic mobility and solvent viscosity, hydrogen bonding ability, dielectric constant and its specific interaction with ions. The influence of various temperatures on conductivity measurement can give detailed information of ion-ion and ion-solvent interaction for different electrolytes solution. Cobalt sulfate heptahydrate is essential for most greater varieties of life, but more than a few milligrams each day is harmful. Rarely possess poisoning come by cobalt substance. After breathing associated with salts, there is some evidence for carcinogenicity. Cobalt sulfate is employed in storages batteries and electroplating baths, sympathetic inks, and as an additive to soils and animal feeds. For these purposes, cobalt sulfate is produced by treating cobalt oxides with sulfuric acid [1-5]. Our purpose is to try to estimate different concentrations of nano copper sulfate to get rid from body and environment and to view the different thermodynamics for nano cobalt sulfate. The synthesis of transition metal complexes with Schiff bases of nitrogen and oxygen donor has stimulated interest due to their vast variety of biological activities ranging from pharmacological, antitumor, fungicide, bactericide, anti-inflammatory, and antiviral activities. These non-covalent interactions can help us for analysis of salts role influence in bodies and environment. There has been much research on complex formation. There are a number of physicochemical techniques that can be used in the study of these complexation reactions, for example, spectrophotometry, polarography, NMR spectrometry, calorimetry, potentiometry and conductometry. Nevertheless of all these techniques, conductometric techniques are the most useful for studying this complexation of complexes. This is because conductometric techniques are highly sensitive and inexpensive.

2. Materials and methods
2.1 Materials
All glassware used was of Pyrex ‘A’ grade quality. Cobalt sulfate heptahydrate (CoSO₄, 7H₂O, E. Merck, 99 % pure), and methanol (CH₃OH) of E. Merck (HPLC grade) were used without further purification. Deionized water was used for preparation of different percentages (0 % to 70 %v/v) of aqueous methanol systems. Digital direct reading conductivity meter model HI-9813, Hanna used to measure the conductivities, having a dip type conductivity electrode with cell constant 1cm⁻¹

2.2 Preparation of nano cobalt sulphate
The ligand Molecular Structure:

![Molecular Formula: C₃H₄N₂O₃S](image)
2.3 Conductometric titration

In a typical experiment, 5 mL of the Calcon CA solution (5.0 x 10^{-3} M) was placed in the titration cell, thermo stated at the preset temperature and the conductance of the solution was measured after the solution reached thermal equilibrium. Then, a known amount of the CoSO_4\cdot7H_2O 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 cation-to-ligand mole ratio was achieved. The specific conductance values were recorded. The conductometer was conducted with a thermostat of the type the Kottermann 4130 ultra thermostat. The temperature was adjusted at 298.15, 303.15, 308.15 and 313.15 K.

3. Results and discussion

TEM Imagies

All imagies 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.

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

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

Where $K_s$ and $K_{solv}$ are the specific conductance of the solution and the solvent, respectively; $K_{cell}$ the cell constant and $C$ is the molar concentration of the CoSO_4\cdot7H_2O solution.

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 2:1, 1:1 and 1:2 [M : L] stoichiometric complexes, Fig (2-5)

From Fig (2-5) addition of the CoSO_4\cdot7H_2O solution to the ligand (Calcon CA) solutions caused a continuous decrease in the molar conductance of the solutions, indicating the lower mobility of the complex cations 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 2:1, 1:1 and 1:2 [M : L] complex between the ligand and the cation solutions used.

The 1:1 binding of the Co^{2+} cations with Calcon CA ligand can be expressed by equilibrium:

$$M^{2+} + L \leftrightarrow ML^{2+}$$

And the corresponding formation constants ($K_f$) for Co^{2+}-Calcon CA complexes were calculated by using equation:

$$K_f = \frac{[ML^{2+}]}{[M]^{2+}[L]}$$ (2)

where $[ML^{2+}],[M^{2+}],[L]$ and $f$ represents the equilibrium molar concentrations of complex, free cation , free ligand and the activity coefficients of the species indicated, respectively.

Under the dilute conditions used, the activity coefficient of the uncharged ligand, $f_l$ can be reasonably assumed to as unity [6, 7]. The use of Debye-Hückel limiting law of electrolytes leads to the conclusion that $f_M = f_l = f_{ML} = 1$, so that the activity coefficients in eq. 2 cancel out.

Thus, the complex formation constant in terms of the molar conductance can be expressed as:

$$K_f = \frac{[ML]}{[M][L]} = \frac{\Lambda_{ML} - \Lambda_{ML}}{(\Lambda_{obs} - \Lambda_{ML})[L]}$$ (3)

$$[L] = C_L - \left\{ C_M + \frac{\Lambda_{ML} - \Lambda_{ML}}{(\Lambda_{M} - \Lambda_{ML})} \right\}$$ (4)
Here, $\Lambda_{M}$ is the molar conductance of the CoSO$_4$.7H$_2$O solution before addition of the ligand, $\Lambda_{ML}$ is the molar conductance of the complex, $\Lambda_{0}$ is the molar conductance of the solution during titration, $C_1$ is the analytical concentration of the ligand, and $CM$ is the analytical concentration of the CoSO$_4$.7H$_2$O solution. The complex formation constant, $K_f$, and the molar conductance of the complex, $\Lambda_{ML}$, were obtained by computer fitting of Eqs. (4) and (5) to the molar conductance- mole ratio data using a nonlinear least-squares program KINFIT[12].

The stability constants of the resulting 2:1, 1:1 and 1:2 [M: L] complexes were determined from the computer fitting of Eqs.3 and 4 to the molar conductance-mole ratio data. A sample computer fit of the mole ratio data is shown in Fig (1) and all $K_f$ values are summarized in Table (1) [13-24].

The Gibbs free energies of formation for each stoichiometric complex were calculated by:

$$
\Delta G_f = -RT \ln K_f
$$

The calculated $\Delta G_f$ values are presented in Table (2).

The enthalpy changes of complexation ($\Delta H_f$) were calculated from the plots of log $K$ against 1/T, (slope = $-\Delta H/2.303 R$) (Fig. 6) using Van’t Hoff's eqn[20-24].

$$
\log K = \frac{-\Delta H}{2.303 R} \left(\frac{1}{T}\right) + \text{constant}
$$

Where R is the gas constant and T is the absolute temperature.

Entropy change $\Delta S$ were for complexes calculated [8] by using Gibbs-Helmholtz equation (6)[31-45]:

$$
\Delta G_f = \Delta H_f - T\Delta S_f
$$

The calculated values of ($\Delta H_f$) and ($\Delta S_f$) for CoSO$_4$.7H$_2$O-Calcon CA stoichiometric complexes are presented in Table (3).

Enthalpies and entropies of complexation reactions show that, a negative value of enthalpic change is also obtained. Comparison of $\Delta H_f$ values of complexation Table (1) clearly revealed that the steric hindrance in organic ligand is an important factor in enthalpy changes in the process of complexation reactions. On the other hand, in most cases, the entropy changes during complexation reactions are quite favorable. The entropic change during the complex formation is in fact affected by several factors including the change in flexibility of the reactants in the course of complexation reaction and the differences between the extent of solvation–desolvation of the uncomplexed and complexed species. The values of $K_f$ decrease with increasing temperature, this may be attributed to the short range interaction and the hydrogen bonding formed at low temperature, also the value of $K_f$ increase as water percentage increase due to H-bonding formation and increasing viscosity.

Interestingly to note, a comparison between the $\Delta S_f$, $\Delta H_f$ and $\Delta G_f$ reported in Table (1) reveals that generally a decrease in $\Delta H_f$ value is accompanied with an increase in $\Delta S_f$ in such a way that the free energy change $\Delta G_f$ will remain more or less constant. Such enthalpy-entropy compensation effect was observed earlier in the case of complexation reactions of ligands with cation and inorganic guest species.

Since the conductance of an ion depends mainly on its mobility, it is quite reasonable to treat the rate process taking place with the change of temperature on the basis of equation (8)[21-24]

$$
\frac{\Delta \sigma}{\Delta \sigma} = A e^{\frac{F E_a}{RT}}
$$

Where A is the frequency factor, R is the gas constant and $E_a$ is the Arrhenius activation energy of the transfer process. Consequently, from the plot of log ($\Delta \sigma$) vs. 1/T, the $E_a$ values can be evaluated, giving high activation energy value due to solvation behavior.
Fig (3) The relation between molar conductance ($\Lambda_m$) and the [M]/[L] molar ratio of nano CoSO$_4$.7H$_2$O to Calcon CA in different aqueous methanol solvents at 303.15 K.

Fig (4) The relation between molar conductance ($\Lambda_m$) and the [M]/[L] molar ratio of nano CoSO$_4$.7H$_2$O to Calcon CA in different aqueous methanol solvents at 308.15 K.

Fig (5) The relation between molar conductance ($\Lambda_m$) and the [M]/[L] molar ratio of nano CoSO$_4$.7H$_2$O to Calcon CA in different aqueous methanol solvents at 313.15 K.
Fig (6) The relation between log Kf for (2:1), (1:1) and (1:2) stoichiometric complexes between nano CoSO₄·7H₂O and Calcon CA against 1/T in pure water.

Fig (7) The relation between log Kf for (2:1), (1:1) and (1:2) stoichiometric complexes between nano CoSO₄·7H₂O and Calcon CA against 1/T in 10% Methanol-water.

Fig (8) The relation between log Kf for (2:1), (1:1) and (1:2) stoichiometric complexes between nano CoSO₄·7H₂O and Calcon CA against 1/T in 30% methanol-water.
The relation between log $K_f$ for (2:1), (1:1) and (1:2) stoichiometric complexes between nano CoSO$_4$.7H$_2$O and Calcon CA against 1/T in 50% methanol-water.

The relation between log $K_f$ for (2:1), (1:1) and (1:2) stoichiometric complexes between nano CoSO$_4$.7H$_2$O and Calcon CA against 1/T in 70% methanol-water.

The formation constants (log $K_f$) of formation for interaction of nano CoSO$_4$.7H$_2$O with Calcon CA complexes in mixed methanol-water at different temperatures.

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The Gibbs free energies ($\Delta G_f$) for interaction of nano CoSO$_4$.7H$_2$O with Calcon CA complexes in methanol-water at different temperatures.

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The enthalpies ($\Delta H_f$) and entropies ($\Delta S_f$) of formation for interaction of nano CoSO$_4$.7H$_2$O with Calcon CA complexes in methanol-water at different temperatures.

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4. Conclusion

This work focused on the study of thermodynamic complexation reactions between the ligand, Calcon CA, with nano Co$^{2+}$metal cation. The stability constants of the complex formation between ligand and metal cations were investigated by applying the conductometric method at different temperatures. Based on the results, the stability constant for the complexation reaction of Co$^{2+}$-Calcon CA shows a decrease with increasing temperatures.

In this thermodynamic study, the negative sign of the $\Delta G_f$ shows that the ligand is capable of forming stable complexes and that the process will proceed spontaneously, while the positive sign of the entropy shows that $\Delta S_f$ is the driving force of the complexation reaction in this complex formation. These facts mean that $\Delta G_f$ is always negative and $\Delta S_f$ is always positive.

References

Electron Donor-Acceptor Interaction Parameters of