

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 CoSO_4 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]. 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

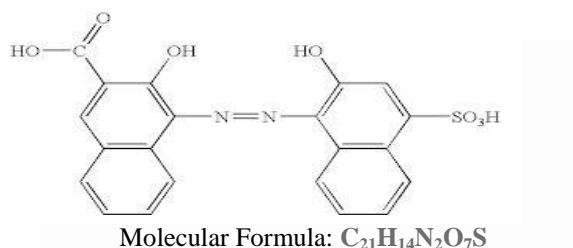
biological activities ranging from pharmacological, antitumor, fungicide, bactericide, anti-inflammatory, and antiviral activities. These non-covalent interactions can help us for analysis of salts role influence in bodies and environment. There has been much research on complex formation. There are 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. Experimental Materials

All glassware used was of Pyrex 'A' grade quality. Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, E. Merck, 99 % pure), and methanol (CH_3OH) 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}

Preparation of nano cobalt sulphate

The ligand Molecular Structure:



Conductometric titration

In a typical experiment, 5 mL of the Calcon CA solution ($5.0 \times 10^{-3} M$) 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 $CoSO_4 \cdot 7H_2O$ solution ($1.0 \times 10^{-3} M$) 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.

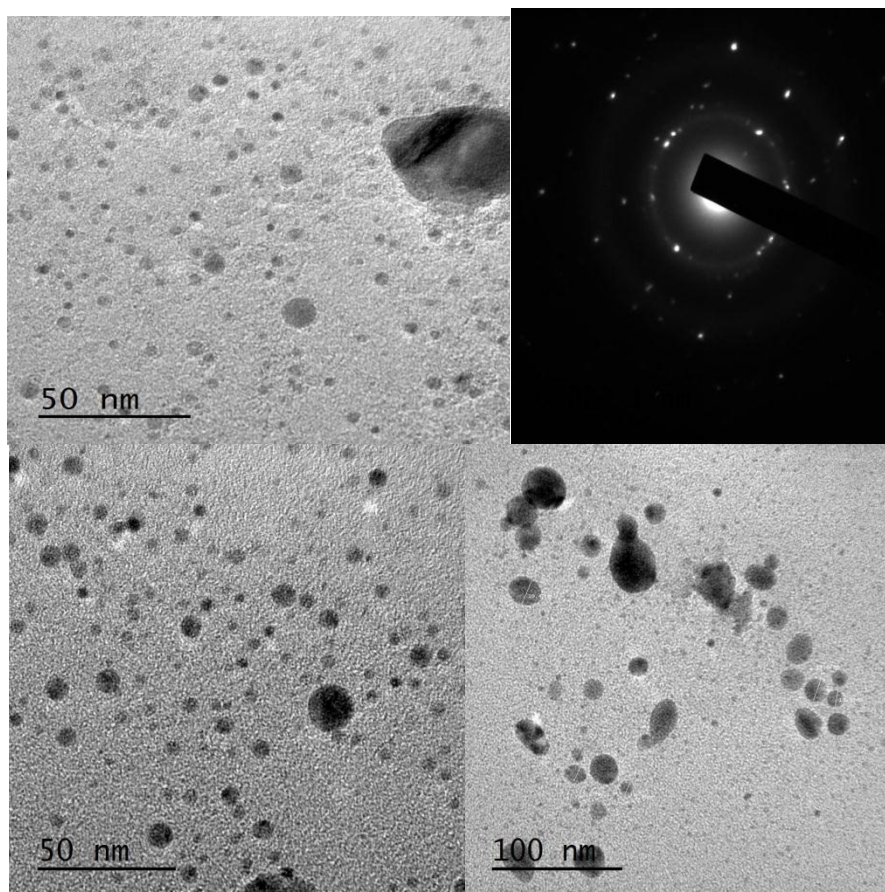


Fig 1. TEM images for nano cobalt sulfate

The molar conductance (Λ_m) values were calculated using equation (1):

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

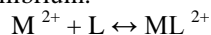
Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} the

cell constant and C is the molar concentration of the $CoSO_4 \cdot 7H_2O$ solution.

By drawing the relation between molar conductance (Λ_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 figs. (2-5) addition of the $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ 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:



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

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

where $[\text{ML}^{2+}]$, $[\text{M}^{2+}]$, $[\text{L}]$ 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 $f_{\text{M}^{2+}} \& f_{\text{ML}^{2+}}$, 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:

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

$$[\text{L}] = C_{\text{L}} - \left\{ C_{\text{M}} + \frac{\Lambda_{\text{M}} - \Lambda_{\text{obs}}}{(\Lambda_{\text{M}} - \Lambda_{\text{ML}})} \right\} \quad (4)$$

Here, Λ_{M} is the molar conductance of the $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ solution before addition of the ligand, Λ_{ML} the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during titration, C_{L} the analytical concentration of the ligand, and C_{M} , the analytical concentration of the $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ solution. The complex formation constant, K_f , and the molar conductance of the complex, Λ_{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 [15-25].

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

$$\Delta G_f = -RT \ln K_f \quad (5)$$

The calculated ΔG_f values are presented in Table (2).

The enthalpy changes of complexation (ΔH_f) were calculated from the plots of $\log K$ against $1/T$, (slope = $-\Delta H/2.303 R$) (Fig. 6) using Van't Hoff eqn. [20-25]

$$\log K = -\frac{\Delta H}{2.303R} \left(\frac{1}{T} \right) + \text{constant} \quad (6)$$

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

Entropy change ΔS were for complexes calculated [8] by using Gibbs-Helmholtz equation (6) [31-45].

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (7)$$

The calculated values of (ΔH_f) and (ΔS_f) for $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ -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 ΔH_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 ΔS_f , ΔH_f and ΔG_f reported in Table 1 reveals that generally a decrease in ΔH_f value is accompanied with an increase in ΔS_f in such a way that the free energy change ΔG_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) [21-25]

$$\lambda \circ = A e^{-\frac{E_a}{RT}} \quad (8)$$

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 $\log (\lambda \circ)$ vs. $1/T$, the E_a values can be evaluated, giving high activation energy value due to solvation behavior.

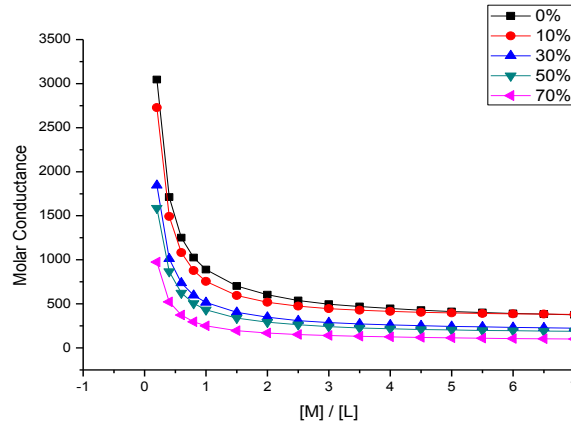


Fig 2. The relation between molar conductance (Λ_m) and the [M]/[L] molar ratio of nano CoSO₄·7H₂O to Calcon CA in different aqueous methanol solvents at 298.15 K.

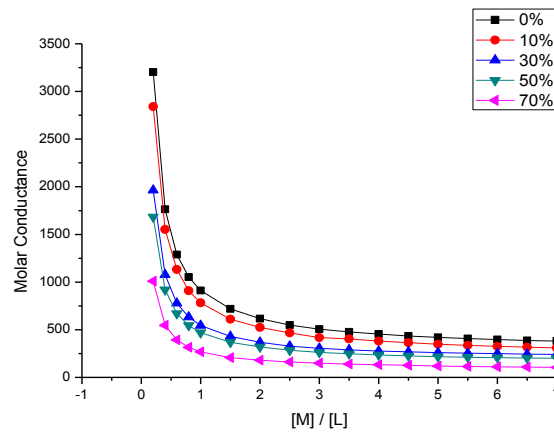


Fig 3. The relation between molar conductance (Λ_m) and the [M]/[L] molar ratio of nano CoSO₄·7H₂O to Calcon CA in different aqueous methanol solvents at 303.15 K.

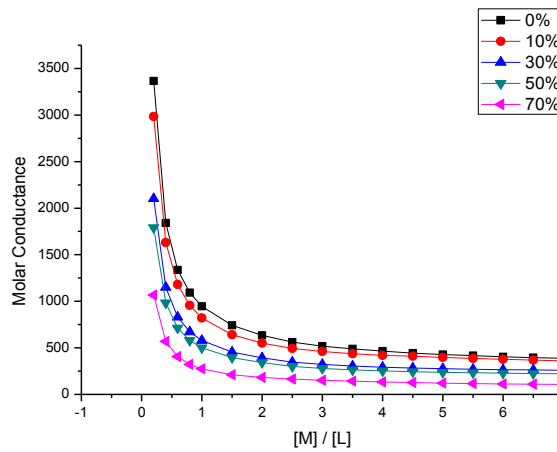


Fig 4. The relation between molar conductance (Λ_m) and the [M]/[L] molar ratio of nano CoSO₄·7H₂O to Calcon CA in different aqueous methanol solvents at 308.15 K.

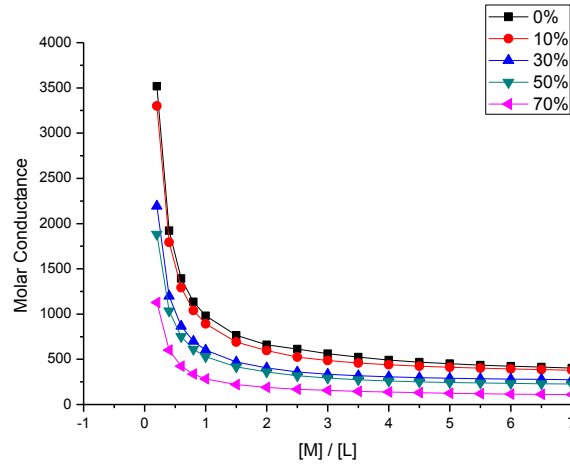


Fig 5. The relation between molar conductance (Λ_m) and the [M]/[L] molar ratio of nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ to Calcon CA in different aqueous methanol solvents at 313.15 K.

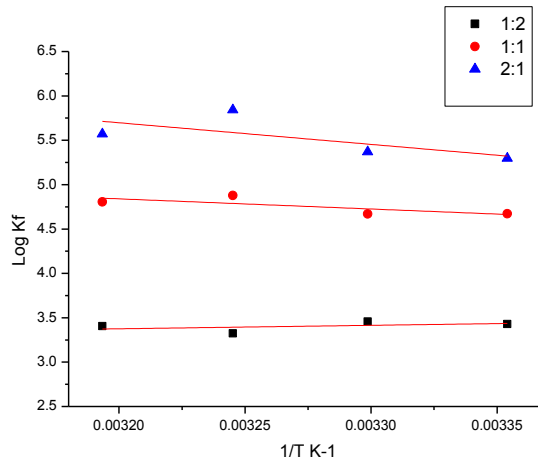


Fig 6. The relation between $\log K_f$ for (2:1), (1:1) and (1:2) stoichiometric complexes between nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and Calcon CA against $1/T$ in pure water.

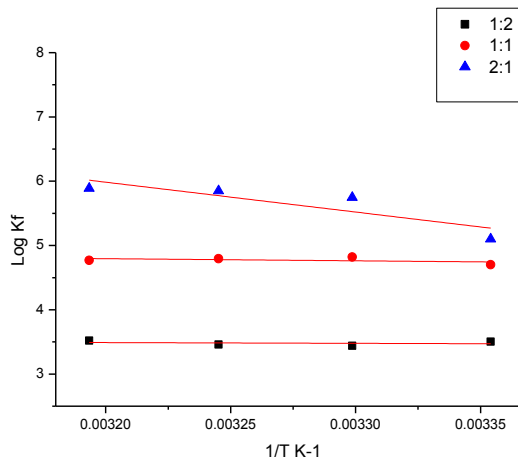


Fig 7. The relation between $\log K_f$ for (2:1), (1:1) and (1:2) stoichiometric complexes between nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and Calcon CA against $1/T$ in 10 % Methanol- water.

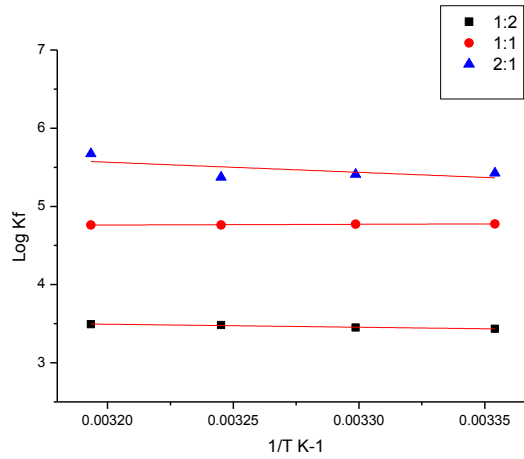


Fig 8. The relation between $\log K_f$ for (2:1), (1:1) and (1:2) stoichiometric complexes between nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and Calcon CA against $1/T$ in 30% methanol- water.

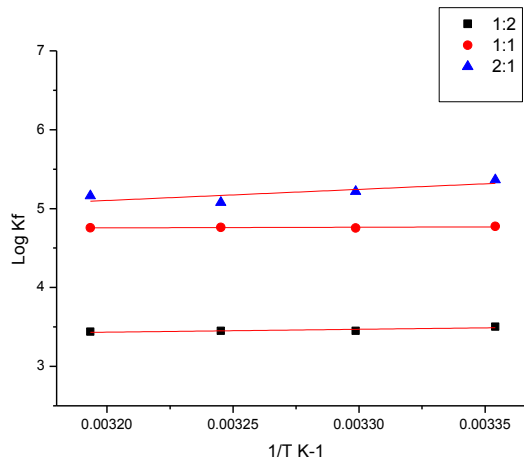


Fig 9. The relation between $\log K_f$ for (2:1), (1:1) and (1:2) stoichiometric complexes between nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and Calcon CA against $1/T$ in 50% methanol- water.

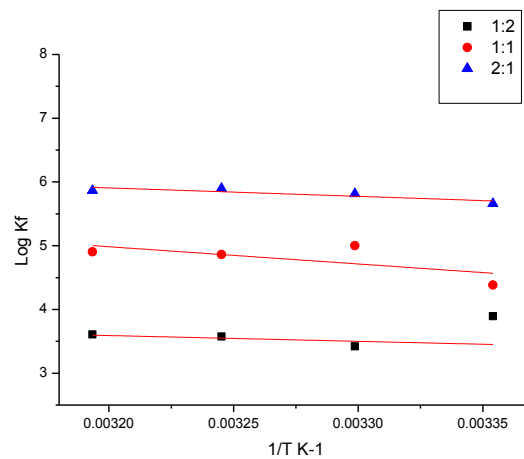


Fig 10. The relation between $\log K_f$ for (2:1), (1:1) and (1:2) stoichiometric complexes between nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and Calcon CA against $1/T$ in 70 % methanol- water.

Table 1. The formation constants ($\log K_f$) of formation for interaction of nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ with Calcon CA complexes in mixed methanol-water at different temperatures.

Vol.% Of MeOH.	$\log K_f$											
	1:2 M:L				1:1 M:L				2:1 M:L			
	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
0	3.4299	3.4570	3.3244	3.4049	4.6726	4.6691	4.8786	4.8062	5.2972	5.3693	5.8415	5.5713
10	3.5050	3.4402	3.4574	3.521	4.7007	4.8212	4.7935	4.7674	5.0994	5.7480	5.8517	5.8878
30	3.434	3.4516	3.4820	3.4927	4.775	4.7728	4.7630	4.7624	5.4264	5.4103	5.3717	5.6737
50	3.5034	3.44932	3.4494	3.4387	4.7743	4.7530	4.7629	4.7567	5.3649	5.2180	5.0778	5.1623
70	3.8941	3.41905	3.5744	3.6080	4.38211	4.9997	4.8617	4.9045	5.661	5.8138	5.8986	5.8675

Table 2. The Gibbs free energies (ΔG_f) for interaction of nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ with Calcon CA complexes in methanol-water at different temperatures.

Vol.% Of MeOH.	$(\Delta G_f) J mol^{-1} K^{-1}$											
	1:2 M:L				1:1 M:L				2:1 M:L			
	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
0	-19.580	-20.066	-19.61	-20.41	-26.674	-27.101	-28.78	-28.81	-30.240	-31.16	-34.46	-33.405
10	-20.00	-19.9687	-20.39	-21.11	-26.8353	-27.984	-28.28	-28.58	-29.1115	-33.36	-34.52	-35.302
30	-19.605	-20.0349	-20.54	-20.94	-27.2641	-27.704	-28.10	-28.55	-30.978	-31.40	-31.69	-34.0192
50	-20.000	-20.0215	-20.35	-20.61	-27.2556	-27.588	-28.10	-28.52	-30.6267	-30.28	-29.96	-30.953
70	-22.23	-19.8457	-21.09	-21.63	-25.0163	-29.020	-28.68	-29.40	-32.3179	-33.74	-34.80	-35.1815

Table 3. The enthalpies (ΔH_f) and entropies (ΔS_f) of formation for interaction of nano $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ with Calcon CA complexes in methanol- water at different temperatures.

Vol.% Of MeOH	1:2 M:L				1:1 M:L				2:1 M:L			
	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
0												
ΔS_f	40.597	41.5290	39.392	41.320	162.910	161.632	164.47	161.95	257.9545	256.75	263.29	255.7046
ΔH_f		-7.47651			21.89683					46.668		
10												
ΔS_f	74.632	73.26737	73.477	74.58	111.2491	113.205	112.33	111.50	396.0468	403.54	400.76	396.8473
ΔH_f		2.242297			6.333632					88.969		
30												
ΔS_f	90.481	90.40584	90.594	90.417	85.42654	85.4686	85.376	85.457	186.9845	185.30	183.24	187.739
ΔH_f		7.37167			-1.79416					24.771		
50												
ΔS_f	43.640	42.99085	43.366	43.524	86.207	85.8843	86.157	86.119	12.1507	10.832	9.5940	12.6105
ΔH_f		-6.98879			-1.55303					-27.00		
70												
ΔS_f	133.04	122.9813	125.02	124.76	257.5402	266.502	261.08	259.22	193.5333	195.05	195.31	193.4075
ΔH_f		17.43606			51.76934					25.384		

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 ΔG_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 ΔS_f is the driving force of the complexation reaction in this complex formation. These facts mean that ΔG_f is always negative and ΔS_f is always positive.

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