Determination of Formation Constants and Thermodynamic Parameters of Chromium (III) Ions with Some Ligands by Conductometry.

Enemo E.R.[1], Ezenwa T.E.[1] and Nleonu E.C.[2]

[1.] *Department of Pure and Industrial Chemistry, Chukwuemeka Odumegwu Ojukwu University, Uli, Anambra State, Nigeria.*
[2.] *Department of Chemistry, Federal Polytechnic Nekede, Owerri, Imo State, Nigeria.*
Corresponding Author: Enemo E.R.

Abstract: *The stability constant and thermodynamic equilibrium stability constant of formation of chromium (III) ions with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ have been determined by conductometric method in aqueous medium at four different temperatures (302,308,313 and 318K). The thermodynamic parameters ΔG, ΔH and ΔS were calculated. The results revealed that Cr (III) ions form a stable complexes with the studied ligands at lower temperature. The thermodynamic data obtained shows fair agreement with the existence and stability of the metal-ligand complexes.*
Keywords: *Stability constant, thermodynamic equilibrium stability constant, thermodynamic parameter, conductometry, metal complexes.*

I.   Introduction

In recent years, the coordination theory has found increasing application in many types of chemical work. Its usefulness in the selection of organic precipitants for metallic ions and in explaining biological phenomena is well known [1]. It is also the basis for our understanding of the role of metal ions in leather tanning, cloth dyeing, plant growth regulation and chelation therapy [1]. The essential metals such as iron, manganese, cobalt and nickel play vital roles in biological processes in form of complexes and their stability contributes to their efficiency [2]. Studies in metal-ligand complexes in a solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would interestingly throw a light on the mode of storage and transport of metal ions in biological kingdom [3].

Complex formation involves disappearance of certain ions in coordination with ligands to form complex compounds. If the stability constant of a reaction between metal and ligand are found to be greater than zero, it's perhaps one of the most convincing evidence for the existence of the complex species [4]. The factors that determine which ligand will coordinate best with a given metal ion are numerous, complicated and not completely understood [5]. The bond between the metal ion and a ligand shows high dependency on the properties of the metal atom. The most of these properties are the size of the metal atom, its ionic charge, atomic number, electronic configuration, electronegativity, and ionization potential [6].

Various types of physico-chemical techniques have been used for the complexometric study such as pH-metry, potentiometry, conductometry, polarography, spectrophotometry, and ion-exchange [7]. Out of these various techniques, conductometry technique is considered as a more accurate technique because it shows high precision at extremely low concentration where the interaction between cation ad anion are influenced and stabilized by hydrosphere and ionosphere formation [8].

Literature survey reveals that the conductometry and thermodynamic study of complex formation have been studied by various researchers [7].

In the present study, thermodynamic equilibrium formation stability constant of chromium (III) ions with cyanide, thiocyanide, ethylene diamine tetraacetic acid, methylamine and ethylamine were studied.

II.   Experimental

Reagents

All the chemicals used are of analytical grade and high purity. The chemical are $CrCl_3$, CH_3NH_3, and $C_2H_5NH_2$, Na_2EDTA, $NaSCN$ and $NaCN$. $0.05M$ of metal solution was prepared by dissolving the requisite quantities in distilled deionised water. Similarly, ligand solution of $0.06M$, $0.04M$, $0.02M$, $0.005M$, and $0.0025M$ concentration of $NaCN$, $NaSCN$, Na_2EDTA, CH_3NH_2, and $C_2H_5NH_2$ were also prepared in distilled deionised water respectively.

CONDUCTANCE MEASUREMENT

The conductance measurements were performed using conductivity meter model, Jenway 4510. Equal volume of 50ml of metal ion solution and ligand solution was mixed together after taking the conductance reading of the metal ion and the conductance reading of the metal-ligand mixture was taken. The readings were recorded. Conductance was used to measure the complexation of the metal-ligand solution at different temperatures of 302, 308, 313 and 318K.

STABILITY CONSTANT

The stability constant of the metal ion – ligand interactions for complex formation using equilibrium reaction between the ligand and the metal ions:

$$M^{m+} + L^{n-} \rightleftharpoons ML^{(m-n)}$$
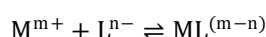
Where M is the metal ion (e⁻ pair acceptor), m is the charge of M; L is the ligand (e⁻ pair donor) and n is the charge of the ligand.

According to the principle of mass action, the activities of M, L, and ML are as follows:

$$K_{ML} = \frac{[ML^{(m-n)}]}{[M^{m+}][L^{n-}]}$$

Where K_{ML} is the equilibrium constant or stability constant. Conductivity method was used to monitor the complex formation of metal and ligand and stability constant can be defined as:

$$K_f = \frac{\propto}{C(1-\propto)^2}$$

Where K_f = stability constant of formation, C is the concentration of the metal ion and, α is the degree of ionisation, where α is determined using the equation as stated below:

$$\propto = \frac{\Lambda}{\Lambda_o}$$

Where Λ is molar conductance and Λ_o is limiting molar conductance [8].

III. Results And Discussion

The metal-ligand stability constant and thermodynamic equilibrium stability constant of formation of Cr (III) ions and CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ were determined in aqueous medium at different temperatures of 302, 308, 313 and 318K respectively.

Metal-ligand stability constant

The limiting molar conductance and stability constant of formation of Cr (III) ions with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ at different temperatures are summarised in Table 1 and 2. The limiting molar conductance shows increase with rise in temperature indicating increase in ionic mobility of the complexed and uncomplexed ions in solution. The high limiting conductance values suggested that all the complexes are electrolytes [9]. It is seen in Table 2 the stability constants of the metal-ligand complexes generally shows formation of stable complexes at lower temperature.

Table 1: The limiting molar conductance of Cr (III) ions with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ at different temperatures.

Complexes	$\Lambda_0 \times 10^6 \mu Smol^{-1}cm^2$			
	302K	308K	313K	318K
Cr-CN	7.07	22.22	23.31	25.24
Cr-SCN	8.09	22.78	26.06	29.04
Cr-EDTA	7.81	35.53	39.36	0.00
Cr- CH_3NH_2	16.56	24.26	25.89	28.07
Cr- $C_2H_5NH_2$	13.29	23.65	24.77	26.25

Table 2: The overall stability constant of Cr (III) ions with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ at different temperatures.

Complexes	302K	308K	313K	318K
	Log K_f			
Cr-CN	10.83	11.10	11.01	11.02
Cr-SCN	11.06	11.09	11.05	11.00
Cr-EDTA	10.57	10.56	0.00	0.00
Cr- CH_3NH_2	11.13	10.95	10.93	0.00
Cr- $C_2H_5NH_2$	11.71	10.85	10.51	10.57

Thermodynamic equilibrium stability constant of formation (K_f^T)

The thermodynamic equilibrium stability constant of a species are the measure of extent of its formation under a particular set of condition. The thermodynamic equilibrium stability constant for the metal-ligand complexes were determined by plotting graph of log K_f against square root of ionic strength $\sqrt{I}$ in which the intercept is K_f^T.

Table 3: log K_f^T of Cr (III) ions with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ at different temperatures.

Complexes	302K	308K	313K	318K
	log K_f^T			
Cr-CN	42.65	42.35	42.05	42.05
Cr-SCN	42.16	41.15	40.55	40.93
Cr-EDTA	42.36	35.08	1.60	0.00
Cr- CH_3NH_2	40.68	67.21	66.96	0.00
Cr- $C_2H_5NH_2$	40.44	64.58	63.72	63.88

The perusal of the data in table 3 shows that thermodynamic equilibrium stability constant of the metal-ligand complexes of Cr (III) ions with CN, SCN and EDTA decreases with increase in temperature while $C_2H_5NH_2$ increases with increase in temperature. The results shows that thermodynamic equilibrium stability constant of metal-ligand complexes that decreases with increase in temperature shows degree of dissociation of ligand while metal-ligand complexes that increases with temperature indicates high degree of ionization between the metal and the ligand [10]. The decrease in log K_f^T with increase in temperature indicates ligand dissociation reaction and their complex formation are exothermic which they shows stable complexes at lower temperature [11,12].

Thermodynamic functions

Stability of complexes depends on reaction energy i.e. thermodynamic stability is concerned with metal – ligand bond energies and stability constants [7]. In order to have a better understanding of the thermodynamic complexation reaction of Cr (III) with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$, the Gibb's free energy (ΔG) contribution to the reaction was investigated on the basis of log K_f^T values using the following equation [9]:

$$\Delta G = -2.303RT \log K_f^T$$

The values of enthalpy change (ΔH) and entropy change (ΔS) were evaluated using the well known relationships. The thermodynamic parameters (ΔG), (ΔH) and (ΔS) are presented in Table 4.

It is evident from the data that all the metal complexes at lower temperature studies were accompanied by negative free energy (ΔG) suggesting that a complexation reaction proceeds spontaneously and the metal complexes are thermodynamically stable. The value of (ΔG) indicates that the reaction process favours complex formation at lower temperature.

The negative enthalpy changes (ΔH) obtained in this study suggest that the metal-ligand bonds are fairly strong and complexation reactions are exothermic in nature [13]. The positive value of ΔH obtained for the complexation of Cr (III) ions with $C_2H_5NH_2$ indicate endothermic nature and explain the effect of ligand on metal-ligand complexation. The enthalpy changes of complexation reaction are mainly due to change in salvation, intermolecular ligand-ligand repulsion and steric deformation of the ligand induced by the bound metal ion [14]. The large variation in ΔH values for the different metal complexes provides clear evidence to the assumption that ΔH value is dependent on the chemical structure of the complexes, based on the strength of the metal-ligand coordination [9].

The observed negative entropy (ΔS) obtained in the present work indicates that the complexes largely retains the primary solvation sphere of the metal ions and positive ΔS obtained in some complexation in this present work indicates the release of bound water molecules from the metal complexes.

Table 4: Thermodynamic parameters of Cr (III) ions with CN, SCN, EDTA, CH₃NH₂ and C₂H₅NH₂ at different temperatures.

Complexes	ΔG kJ/mol	ΔH kJ/mol	ΔS kJ/molK
Cr-CN			
302 K	-246.56	-71.46	0.58
308 K	-249.72	-71.08	0.58
313 K	-251.90	-70.36	0.58
318 K	-256.00	-71.56	0.58
Cr-SCN			
302 K	-237.95	-148.26	0.30
308 K	-242.60	-147.12	0.31
313 K	-242.98	-149.08	0.30
318 K	-249.18	-147.42	0.32
Cr-EDTA			
302 K	-244.88	-555.67	-1.03
308 K	-206.83	-554.87	-1.13
313 K	9.63	-557.53	-1.81
318 K	0.00	-556.50	-1.75
Cr- CH₃NH₂			
302 K	-235.21	-394.54	-0.53
308 K	-396.47	-398.48	-0.01
313 K	-400.75	-394.49	0.02
318 K	9.02	-394.86	1.27
Cr- C₂H₅NH₂			
302 K	-233.78	238.40	1.56
308 K	-398.47	239.09	2.07
313 K	-381.81	237.93	1.98
318 K	-388.88	237.58	1.97

Activation energy of the metal-ligand complexes

The activation energy (E_a) of the metal-ligand complex can be treated on the rate process taking place with the change in temperature on the basis of limiting molar conductance (Λ_0) since the conductivity of ions depends mainly on its mobility [15].

$$\Lambda_0 = Ae^{E_a/RT}$$

$$\ln \Lambda_0 = \ln A - \frac{E_a}{RT}$$

Consequently, from the plot of Λ_0 against $\frac{1}{T}$, E_a values were evaluated from the slope. The activation energy values of Cr (III) ions with studied ligands are tabulated in Table 5. The E_a of Cr-EDTA complexation gave a negative value while other metal-ligand complexes were positive. The negative E_a obtained indicates decrease in limiting molar conductance with increase in temperature. It may be attributed to multistep mechanism involved during metal-ligand complexation or due to high degree of dissociation at higher temperature. The metal complexes with positive E_a were in supported the increase in molar conductance with increase in temperature.

Table 5: Activation Energy (E_a) of Metal –Ligand Complexes

Ions	Ligands	Activation Energy (KJ/mol)
Cr³⁺	CN	57.13
	SCN	58.47
	EDTA	-663.29
	CH₃NH₂	24.47
	C₂H₅NH₂	30.97

IV. Conclusion

The results obtained from the conductometric measurements on the thermodynamics of complexation of Cr (III) ions with CN, SCN, EDTA, CH₃NH₂ and C₂H₅NH₂ at different temperatures shows that K_f and K_f^T favours stable complexes at lower temperature. The present work describes the effect of temperature and nature of ligands on the stability of the complexes.

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CONFLICT OF INTEREST
The authors have not declared any conflict of interest.

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