Chemistry Research Journal, **2021, 6(3):112-116**

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Conductometric Study on the Stability Constants and Thermodynamic Parameters of Fe^{3+} Complexes with some Ligands

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

[1]Department of Chemistry, Federal Polytechnic Nekede, Owerri, Imo State, Nigeria
[2]Department of Pure and Industrial Chemistry, Chukwuemeka Odumegwu Ojukwu University, Uli, Anambra State, Nigeria.
Corresponding Author: enleonu@yahoo.com; ORCID No: 0000-0003-4083-2226

Abstract The stability constants and theymodynamic parameters of Fe^{3+} complexes with cyanide, thiocyanide, ethylene diamine tetraacetic acid, methylamine and ethylamine were studied by conductometric method in aqueous medium at different temperatures (302, 308, 313 & 318K). The stability constants and thermodynamic parameters of the metal-ligand complexes were studied at low concentration of the metal and ligand. The results indicated that, the complex formation is spontaneous, exothermic and entropically favourable. The complexes were observed to be stable at lower temperature of the study. The study provides stability constants of iron (III) ions with methyl amine, ethylamine and thiocyanide which are limited in literature.

Keywords Stability constants, thermodynamic parameters, metal-ligand complexes, conductometry

Introduction

Complexation studies are very important for analytical and biochemical researchers in a wide variety of areas like metal ions in biology, biomedical applications, environments, extraction metallurgy, food chemistry and many industrial processes [1,2]. The extent to which the ligands bind to a metal ion is expressed in terms of stability constants [3] and its major application is in chelation therapy. The accurate determination of stability constants values is fundamental in understanding the behaviour of ligands and their interaction with metal ions in solution [2]. The most convincing evidence for the existence of complex species in aqueous solution is when the stability constants of the complexes are found to be greater than zero [4].

The extensive work in co-ordination complexes have been made possible with the help of various experimental techniques [5]. It was of interest to us to determine the stability constants and thermodynamic parameters of iron (III) ion complexes with CN-, SCN- and EDTA using conductometric method because the method is less reported in the literature and their calculation is also simple. Conductometry technique is considered as a more accurate technique in study of metal and ligand complexation because of its high precision at extremely low concentration where the interaction between cation and anion are influenced and stabilized by hydrosphere and ionosphere formation [4,6].

Experimental

Reagents

All the chemicals used are chemically pure analytical grade and were used without further purification. The chemicals are sodium cyanide, sodium thiocyanide, sodium ethylene ditatraacetic acid, methyl amine and ethyl amine. 0.05*M* of metal solution was prepared by dissolving the requisite quantities in distilled deionised water. Similarly, ligand solution of 0.06*M*, 0.04*M*, 0.02*M*, 0.005*M*, and 0.0025*M* 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 carried out 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 before taking the conductance reading of the metal-ligand mixture. The conductance readings of the metal-ligand solution were also taken at different temperatures of 302, 308, 313 and 318K respectively.

Determination of Stability Constant

The stability constant of formation K_f was determined using the method described in our previous publication without modification [4].

Results and Discussion

Metal-Ligand Stability Constant

The stability constant of formation (K_f) for the reaction of Fe^{3+} ions in the presence of CN^-, SCN^-, $EDTA^{2-}$, CH_3NH_2 and $C_2H_5NH_2$ in aqueous medium at temperature of 302, 308,313 and 318k were investigated using conductometric method.

Table 1: Metal-ligand stability constants of Fe^{3+} ions in with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ at Four different temperatures.

	$\log K_f$			
Complexes	**302K**	**308K**	**313K**	**318K**
Fe-CN	10.87	11.06	11.01	11.28
Fe-SCN	10.73	10.91	10.96	10.97
Fe-EDTA	11.94	23.89	0.00	0.00
Fe- CH_3NH_2	10.91	10.97	10.88	10.95
Fe- $C_2H_5NH_2$	10.71	10.7	10.33	10.75

The perusal of the stability constant in table 1 shows that increase in temperature does not have a significant difference in the stability constant for the reaction of Fe^{3+} ions with CN, SCN, CH_3NH_2 and $C_2H_5NH_2$. The high stability constant of the complexes may be attributed to high degree of ionisation between the metal-ions and the ligands. The metal-ions shows no formation of complexes with EDTA after 308k which may be attributed to high degree of dissociation of ligand or non interaction of the metal and the ligand at high temperature.

Thermodynamic Equilibrium Stability Constant

The thermodynamic equilibrium stability constant K_f^T for the metal-ligand complexes were determined using the method earlier reported [4].

Table 2: Log K_f^T of Fe^{3+} ions with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$ at different temperatures

	$\log K_f^T$			
Complexes	**302K**	**308K**	**313K**	**318K**
Fe-CN	42.18	42.07	42.16	43.06
Fe-SCN	42.45	41.71	41.71	41.63
Fe-EDTA	39.69	35.05	1.80	0.00
Fe- CH_3NH_2	42.33	67.14	66.40	66.61
Fe- $C_2H_5NH_2$	42.25	64.49	60.74	64.96

It is seen from Table 2 that the metal-ligand complexes Fe^{3+} with CN shows a low value of K_f^T at 308K. Fe^{3+} ion complexes with SCN and EDTA K_f^T values decreases with temperature while complexes with CH_3NH_2 and $C_2H_5NH_2$ shows greater stability at higher temperature. This phenomenon was observed with Cr^{3+} complexes with the same studied ligands [4]. The low thermodynamic equilibrium stability constant of formation between iron(III) ions and EDTA at 313 and 318K may be attributed to slow displacement of water molecules by EDTA into inner sphere of $[Fe(H_2O)_6]^{3+}$ [7] or attributed to steric hindrance preventing the formation of a square planer structure [8].

Thermodynamic Functions

In order to have a better understanding of the thermodynamic complexation reaction of Fe(III) ions with the studied ligands, the following thermodynamic parameters: ΔG°, $\Delta H^{\circ}$and ΔS° were determined using the well known relationships as described elsewhere [4]. The thermodynamic parameters results are summarized in Table 3.

Table 3: Thermodynamic parameters of Fe^{3+} ions with CN, SCN, CH_3NH_2 and $C_2H_5NH_2$ at different temperatures

Complexes	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/molK)
Fe-CN			
302 K	-245.42	-71.46	0.58
308 K	-248.06	-69.42	0.58
313 K	-252.63	-71.09	0.58
318 K	-262.14	-71.34	0.60
Fe-SCN			
302 K	-245.41	-93.11	0.50
308 K	-245.91	-91.91	0.50
313 K	-248.49	-91.99	0.50
318 K	-253.44	-94.44	0.50
Fe-EDTA			
302 K	-229.46	-528.84	-0.99
308 K	-206.68	-530.08	-1.05
313 K	10.70	-527.66	-1.72
318 K	0.00	-527.88	-1.66
Fe- CH_3NH_2			
302 K	-244.76	-96.98	0.48
308 K	-394.35	-95.59	0.97
313 K	-396.55	-96.07	0.96
318 K	-405.49	-97.03	0.97
Fe- $C_2H_5NH_2$			
302 K	-244.28	219.16	1.53
308 K	-380.27	217.25	1.95
313 K	-369.93	218.51	1.88
318 K	-395.44	218.83	1.93

The negative values of ΔG° revealed that the complex formation is a spontaneous process and the metal chelates are thermodynamically stable. The values of free energies of formation of the complexes becomes less negative with increase in temperature indicating that the complexes are stable at lower temperature. The zero value of ΔG°obtained at 318K for the complex reaction of Fe^{3+} with EDTA shows that the concentration of metal ions and ligand are in equilibrium.

The ΔH values indicate the exothermic nature of complexation reaction of Fe^{3+} ions with CN, SCN, EDTA and CH_3NH_2 while Fe^{3+} with $C_2H_5NH_2$ shows an endothermic nature. The enthalpy change explained the effect of ligand and temperature on the values of formation constants. The entropy values indicates a highly solvated metal complexes and indicated that the formation of these complexes was entropy favoured [9].

Table 4: Activation Energy of Metal-ligand complexes

Complexes	**Activation Energy (KJ/Mol)**
Fe-CN	42.94
Fe-SCN	38.07
Fe-EDTA	-693.99
Fe-CH_3NH_2	11.87
Fe-$C_2H_5NH_2$	8.72

The activation energy (E_a) values of the studied metal-ligand complexes are shown in table 4. The negative E_a obtained for Fe-EDTA complex may be attributed to high degree of dissociation at higher temperature indicating an equilibrium reaction between Fe^{3+} ions and EDTA while the positive activation energy of other complexes shows stability of the complexes.

Conclusion

This paper reports conductometric studies on the stability constants and thermodynamic parameters of Fe^{3+} complexes with CN, SCN, EDTA, CH_3NH_2 and $C_2H_5NH_2$. The results obtained shows thermodynamic stability of the metal-ligand complexes at low temperature and the reactions are spontaneous in nature. The stability constant results suggest the effect of ligand preference by the metal ion.

Acknowledgement

The authors are thankful and express their extreme pleasure to Prof. A.I. Onuchukwu for his valuable guidance towards the actualization of this experimental work. We are also thankful to the Department of Chemistry, Federal Polytechnic Nekede, Owerri, Imo State – Nigeria for providing laboratory facilities.

Conflict of Interest

The authors have not declared any conflict of interest.

References

[1]. Omar A.A. and Ali E.A. (2015). Stability Constants and Stoichiometries of Chromium and Zirconium Carboxylates Complexes Calculated by Four Comparative Methods. *International Journal of Advanced Chemistry*, 3(1): 6-13.

[2]. Ansari F.B., Mansoor F. and Quadiri S.H. (2008). Potentiometric Determination of Stability Constants of Transition Metal Complexes with p-Aminobenzoic Acid. *Int. J. Chem. Sci.*, 6(2): 873-877.

[3]. Sanjay U., PalaskSar N.G. and Farooqui N. (2002). Effect of Temperature and Media on Complexation of Sm (III) with 5-bromo-2-hydroxy Acetophenone. *Asian Journal of Chemistry*, 14(1): 99-102.

[4]. Enemo E.R., Ezenwa T.E. and Nleonu E.C. (2019). Determination of Formation Constants and Thermodynamic parameters of Chromium (III) Ions with some Ligands by Conductometry. *IOSR Journal of Applied Chemistry*, 12(10): 54-58.

[5]. Meshram Y.K., Khan R.F. and Dharamker R.R. (2014). Metal-Ligand Stability Constants of Co(II), Ni(II), Cu(II) Metal ion Complexes with Substituted ketones & Simple Ketones at 0.1M Ionic Strength pH Metrically. *Indian Journal of Applied Research*, 4(3): 37-41.

[6]. Onuchukwu A.I. (2008). Electrochemistry in Electrochemical Technology. Spectrum Books Limited, Ibadan, 3-40.

[7]. Grzybkowski W. (2006). Nature and properties of Metal Cations in Aqueous Solution. *Polish J. of Environ. Stud.*, 15(4): 655-663.

[8]. Basavaraj M.K., Suvarnakhandi S.S., Sheth R.C., Hiremath P.S. and Kalashetti M.B. (2011). Temperature effect on Solution Stability Constants of metal Complexes with Schiff bases Derived from 5-

Aldehydosalicylic Acid – Anilline and its related Compounds. *International Journal of Applied Biology and Pharmaceutical Technology*, 2(2): 88-93.

[9]. Gouda G.A.H., Ali G.A.M and Seaf Elnasr T.A. (2015). Stability Studies of Selected Metal Ions Chelates with 2-(4-amino-1,5-dimthyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino) Phenol. *Int. J. Nano. Chem.*, 1(2): 39-44.