www.ThePharmaJournal.com

The Pharma Innovation

Vivek Kumar
Department of Chemistry, J.V. Jain (P.G.) College, Saharanpur, Uttar Pradesh, India

Raj Kumar
Professor and Head, Department of Chemistry, J.V. Jain (P.G.) College, Saharanpur, Uttar Pradesh, India

Equilibrium studies of complexes of Fe (III) and Co(II) potassium Propan-1,3-Diol Di Xanthate

Vivek Kumar and Raj Kumar

Abstract
Equilibrium constant or stability constant is used to determine the strength of interaction between reagents that make the final product after the formation of bonds. In general, stability means that a complex may be stored for a long time under suitable conditions or the compound may be existing under suitable conditions. Regarding how much is the concentration of complexes in solution, stability constant provides this information via calculations. These calculations are very important in many areas of science like chemistry, biology, and medicine. Stability of metal complexes may be affected by various factors like nature of central metal ion and ligand, chelating effect etc. In this study at different ionic strengths and temperatures, such as 25 °C, 30 °C, and 35 °C, overall stability constants (log K) of the complexes were obtained and thermodynamic stability constants (log K°) at zero ionic strength were derived for each metal system for log K vs ionic strength plots.

Keywords: Complex, equilibrium constant, thermodynamic properties, entropy

Introduction

A stability constant (formation constant, binding constant) is an equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. There are two main kinds of complex: compounds formed by the interaction of a metal ion with a ligand and supramolecular complexes, such as host–guest complexes and complexes of anions. The stability constant provide the information required to calculate the concentration of the complexes in solution. There are many areas of application in chemistry, biology and medicine. The larger the value of equilibrium constant the more stable is a complex ion.

Babanly [1] studied some issues of complex studies of phase equilibria and thermodynamic properties in ternary chalcogenide systems involving emf measurements. The formation equilibria of the complexes of some transition metal ions and triazolylazonaphthol (TAN) have been investigated by a Shoukry [2] *et al*. The stepwise formation constants of the complexes formed in solution were calculated using the non-linear least-squares computer program MINIQUAD. The concentration distribution of the complex species was resolved. Complexes of Cu(II), Co(II), Ni(II), Cd(II), Zn(II), UO_2(VI) and Pd(II) have been synthesized and characterized by elemental analyses, electrolytic conductance, spectral and magnetic measurements. The ligand forms 1:2 complexes (metal ion: ligand), except for Pd(II), where 1:1 complex is formed. The Ni(II) and Co(II) complexes are octahedral and of the general formula ML_2, where L is the uninegatively charged tridentate ligand (ONN donor set). The Cu(II) complex is binuclear with a ligand-bridged structure.

Akat [3] el al uses method of pH metrically chemical equilibrium studies of transition metal complexes of Ca(II), Cu(II) and Cr(II) transition metal ions with Lamivudine (3CT) drug (D) and a series of eight amino acids (A) have been investigated at 300C temperature and 0.1 Molar ionic strength Sodium perchlorate ($NaClO_4$) in aqueous solution. During reaction formation of various possible complex species had been evaluated and analysed by using the special computer program and discussed in terms of various relative stability parameters. By using Calvin and Bjerrum as Proton ligand stability constants (pKa) and metal ligand stability constants (Log K) of metal complexes were determined the method which was as modified by Irving and Rossetti methods at various temperatures.

Kanahashi [4] studied machine learning-based analysis of overall stability constants of metal–ligand complexes. The stability constants of metal(M)-ligand(L) complexes are industrially important because they affect the quality of the plating film and the efficiency of metal separation.

Corresponding Author:
Vivek Kumar
Department of Chemistry, J.V. Jain (P.G.) College, Saharanpur, Uttar Pradesh, India

Thus, it is desirable to develop an effective screening method for promising ligands. The electronegativities of both metal and ligand are found to be the most important factor for predicting the first overall stability constant. Interestingly, the predicted value of the first overall stability constant shows the highest correlation with the nth overall stability constant of the corresponding M-L pair. Finally, the number of features is optimized using validation data where the ligands are not included in the training data, which indicates high generalizability. This provides valuable insights and may help accelerate molecular screening and design for various applications.

Materials and Methods
PPDDX Solution
By dissolving the weighed amount of the material in double distilled oxygen free water, the solution of necessary strength of PPDDX was prepared. Fresh solution of PPDDX was prepared daily.

The metal salt solutions (Ferric chloride, Cobalt chloride, and Potassium chloride) were prepared according to the instructions given below.

Ferric chloride
Anhydrous ferric chloride (A.R.) was dissolved to make ferric chloride solution. After reducing Fe(III) to Fe(II) using ferroin as an indicator, the strength of the solution was evaluated volumetrically [5] using Ce(IV) sulphate. Dilution was used to create solutions of the desired strengths.

Cobalt chloride
The appropriate quantity of Co(II) chloride (A.R.) stock solution was made by dissolving it in doubly distilled water. Gravimetrically [6], cobalt was estimated as tetrathiocynato mercurate(II) (mercurithiocyanate). Diluting the stock solution with the required volume of doubly distilled water to obtain the desired strength solutions.

Potassium chloride
The strength of a stock solution of potassium chloride was determined gravimetrically as chloride by dissolving (A.R. Grade) salt in doubly distilled water.

Prior to doing experiments for spectrophotometric stoichiometric determination of the complex, absorption experiments with metal salts solution and ligand at various wavelengths are carried out to determine the best suitable wavelength range. The number of complexes produced is then determined using Vosburgh-Cooper's technique. Equimolar metal and ligand are synthesized in appropriate solvents and mixed in a metal-to-reagent ratio of 1:1, 1:2, 1:3, 2:1 or 3:1. The mole ratio approach is also used to determine the complexes stoichiometry.

Stability constants determination
Several methods for determining the stability constants of complexes in aqueous and non-aqueous media utilizing absorbance measurements are available. Here's a brief overview of the many approaches.

It is necessary to know the complex formation system in order to fully understand the stability constant. To understand the stability constants of complexes, there are two primary approaches. The concept of ionic strength was first presented by Lewis and Randall [7] and it was later theoretically justified by the Debye Huckel theory [8]. The traditional method for determining thermodynamic equilibrium constants involves determining the equilibrium constant in a variety of mediums with varying ionic strengths, then extrapolating to zero ionic strength.

The second approach was introduced by Biedermann and Sillen [9] and the basic idea is to manage the activity coefficient by keeping the ionic strength constant, because the activity coefficient of a given strong electrolyte in dilute solutions is same across all solutions of identical ionic strength. It is better to achieve valid stoichiometry values using solvent molecules and medium ions, according to Rossotti and Ross [10]. Though it does not give absolute stability, it is appropriate for solvated molecular stability.

The stability constants were calculated using the mole ratio approach at various ionic strengths in the present studies. Below is a quick description of the mole-ratio approach.

Mole Ratio Approach
Consider the following scenario for complex dissociation: -
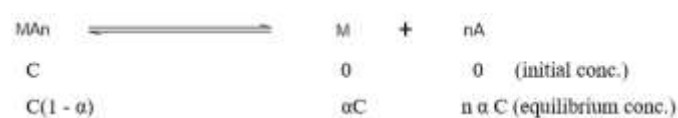
Here 'C' is the total concentration of the complex ion in moles per litres, assuming there isn't any dissociation. The stability constant k can be written as follows:

$$K = C(1-\alpha) / \alpha C \times (n\alpha C)^n \qquad ....(1)$$

The value of 'n' for the complex has been determined and the value of α can be calculated using the mole ratio curve, using the relation

$$\alpha = \frac{E_m - E_s}{E_m} \qquad .....(2)$$

Where 'E_s' is the extinction of the stoichiometric molar ratio of metal to reagent in the complex and 'E_m' is the maximum extinction determined from the horizontal portion of the curve.

Mole Ratio Procedure
The mole ratio was calculated by adding varying volumes of equimolar ligand solution to a constant volume of metal ions in two separate sets. With 1.0 M KCl, the ionic strengths were maintained (*viz.*, 0.05, 0.10, 0.20 M). Each solution was made upto a volume of 10.0 ml with distilled water and thermostated at 25 °C, 30 °C and 35 °C.

The solutions were maintained at these temperatures until they reached a stable temperature. Spectronic-20 was used to do the optical density measurements.

Stability constants were determined using equations 1 and 2 at various temperatures and ionic strengths. Plots of log K vs ionic strength were used to calculate the values of the thermodynamic constant (log K°) at each temperature.

Thermodynamic Parameters
Log K° values were plotted against T^{-1} for each metal-ligand system to calculate the heat of association using least square plot [11-12] of log K° versus T^{-1}. At various temperatures, the change in free energy for each metal-ligand system was

calculated using the well-known equation $\Delta G° = -2.303 RT \log K°$. The $\Delta C_p°$ values were calculated based on the log $K°$ versus T^{-1} graphs nature.

Table-1: Overall stability constants (log K) at different temperatures and ionic strengths (l,mol dm^{-3}) and thermodynamics parameter

System	Temp. (°C)	log K			log K°	ΔG° KJmol^{-1}	ΔH° KJmol^{-1}	ΔS° KJmol^{-1}
		I= 0.05	I = 0.10	I = 0.20				
Fe^{III}-PPDDX	25	4.51	4.43	4.33	4.56			
	30	4.50	4.40	4.31	4.48	-30.7	-25.4	10.3
	35	4.44	4.33	4.24	4.41			
Co^{II}-PPDDX	25	3.42	3.36	3.22	3.50			
	30	3.38	3.32	3.17	3.46	-24.7	-11.5	35.6
	35	3.33	3.26	3.12	3.41			

Results and Discussions
Wavelength for maximum absorption
The maximum absorption of ferric chloride aqueous solution was recorded in the ultra violet region, while no maximum was observed in the visible region. In the visible spectrum of cobalt chloride, there was only one peak observed at 550 nm.

Complexes nature and wavelength selection
The following interesting facts were observed using Vosburgh and Cooper's method for the mixture (metal to PPDDX as 1:1, 1:2, 1:3, 2:1, 3:1) at different wavelengths using equimolar solutions of the reactants.

At low concentrations of the reactants, Fe(III) and Co(II) formed brownish red and dark green soluble complexes and close observation of the Vosburgh - Cooper's curve revealed that the metal ions maximum values had disappeared and possibly moved in the ultraviolet region, except in the case of the cobalt system, where the maximum value of the Co(II) metal ion was shifted. The formation of complexes was indicated by a change in colour and a maximum value of the metal ions. Furthermore, all of the curves corresponding to the various placements of metals and PPDDX are found to be similar in character, implying that just one complex forms in the visible region. It was also discovered that all of the complexes absorbed significantly at high concentrations in the wavelength range of 480 - 520 nm. Optical density data, on the other hand, were adjusted for metal ion absorbance. As a result, the wavelength range (480-520 nm) was chosen for other spectrophotometric analyses.

Composition of the complexes
The stoichiometry of the coloured complexes was determined using Job's method of continuous variation. Job's technique was used to mix and shake equimolar solutions of metal salts (Ferric chloride and Cobalt chloride) and PPDDX. Optical density measurements were taken at various wavelengths and with different reactant concentrations. Wherever appropriate, the optical density of the metal salts, i.e. blank metal was observed. The mixture's corrected optical density was plotted versus the mole fraction, i.e. (M) / (M) + PPDDX, where M= Fe^{+++} and Co^{++}. In all cases, the curves revealed maximum absorption at a mole fraction closed to 0.50, indicating a 1:1 metal - PPDDX ratio. Mole ratio curves have the same stoichiometry as well.

The overall stability constant of the complexes was determined using mole ratio methods at various ionic strengths (0.05, 0.10, 0.20 M maintained by KCl) and at temperatures (25°, 30° and 35 °C) using two distinct reactant concentrations. The effect of wave lengths on the stability value was also found to be negative. However, for each metal, details are only given for three ionic strengths and at one temperature and details for the other sets have been ignored. The table-1 contains values of stability constants at all temperatures and ionic strengths.

For each metal-ligand system at each temperature [13-14], the average values of stability constants were plotted against ionic strengths. The value of the thermodynamic stability constant (log K°) at zero strength was obtained by extrapolating linear curves.

Conclusion
At different ionic strengths and temperatures, such as 25 °C, 30 °C, and 35 °C, overall stability constants (log K) of the complexes were obtained and thermodynamic stability constants (log K°) at zero ionic strength were derived for each metal system for log K vs ionic strength plots. The stability constants were observed to reduce as temperature and ionic strength increased. The present complexes stability was also observed according to the Irving-William order Fe<Co<Ni<Cu. Negative ΔG° and ΔH° values indicated that the metal - ligand interaction was spontaneous and exothermic. Positive ΔS° readings indicated that the complexes were chelated.

References
1. Babanly MB, Mashadiyeva LF, *et al*. Some Issues of Complex Studies of Phase Equilibria and Thermodynamic Properties in Ternary Chalcogenide Systems Involving Emf Measurements (Review). Russ. J Inorg. Chem. 2019;64:1649-1671.
2. Shoukry MM, Hadi AK, Razik AA, Shouheib SM. Synthesis and Equilibrium Studies of the Metal Complexes of Heterocyclic Azo Compounds. 1996;26(3):493-507.
3. Akat GB, Magare BK. Mixed ligand stability constant complex equilibrium study of Lamivudine drug with Ca (II), Cu(II) and Cr(II) transition metal ions Bull. Env. Pharmacol. Life Sci. 2022;(1):794-798.
4. Kanahashi K, Urushihara M, Yamaguchi K. Machine learning-based analysis of overall stability constants of metal–ligand complexes. Sci Rep. 2022;12:11159.
5. Vogel I. Quantitative Inorganic Analysis, IVth ed.; c1968. p. 322.
6. Vogel I. Quantitativa Inorganic Analysis, IVth ed.; c1969. p. 461.
7. Lewis GN, Randall M. The activity coefficient of strong electrolytes. Journal of the American Chemical Society. 1921;43(5):1112-1154.
8. Izatt RM, Haas CG, Fernelius WC. Studies on Coordination Compounds: Calculation of

Thermodynamic Formation Constants at Varying Ionic Strengths. J Phys. Chem. 1954;58:1133-1136.

9. Biedermann G, Sillen LG. The hydrolysis of metal ions. Liquid-junction potentials and constancy of activity factors in $NaClO_4$-$HClO_4$ ionic medium. Ark. Kemi. 1953;5(40):425.

10. Rossotti EJC, Ross H. The determination of stability constants. Mcrgraw Hill, New York; c1961.

11. Kalina DG, Mason GW, Horwitz EP. The thermodynamics of extraction of U(VI) and Th(IV) from nitric acid by neutral phosphorus-based organic compounds, Journal of Inorganic and Nuclear Chemistry. 1981;43(1):159-163.

12. Nair VKS, Nancollas GH. Thermodynamics of ion association. J Chem. Soc; c1959. p. 3934-3939.

13. Irving H, Williams RJP. The stability of transition-metal complexes J Chem. Soc. 1953, 3192-3210.

14. Shah NR, Shah JR. The effect of ligand field splitting on thermodynamic properties of Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) chelates of some 4-oximino-2-pyrazolin-5-ones Journal of Inorganic and Nuclear Chemistry. 1981;43:1583.