DETERMINATION OF STABILITY CONSTANT OF Fe(II) BIPYRIDINE COMPLEX

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Abstract. In this paper the stability constants of Fe(II) complexes were studied using spectrophotometric method. Job's plot was used to evaluate the stability constants of complexes in aqueous media. Experiments shown that obtained result matches well with literature values elsewhere. Factors affecting the determination values also discussed and

Keywords: coordination complex, iron(II), bipyridine, stability constant.
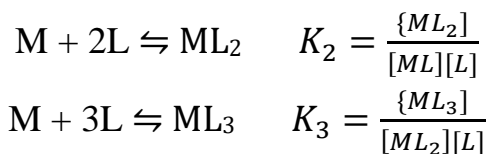
Introduction

Understanding of the formation of metal complexes in an aqueous medium is not a simple and stability constant is more frequently used to evaluate the strength of interaction between metal and ligand bonds [1]. Stability means that a coordination complex may be stored for a long time under suitable conditions. Several factors affects to the stability of metal complexes as nature of central metal ion and ligand, chelating effect, nature of solvents, etc. [2-5].

During the displacement reaction of metal complex formation, some ions substitute their place and form a bonding between metal ions and ligands.

Various modern techniques are used to determine the stability constant of homoleptic or heteroleptic coordination complexes. In a potentiometric technique a sudden pH change was used to calculate stability constant [6]. In other study, a considerably simple method – metal salt solubility was employed [7]. The limitations of the above mentioned method originate from its applicability to ML systems.

As mentioned before, stability constant is applicable to measure the strength of interactions between the ligands and metal ions that are involved in complex formation in the solution. These set of equations describe the formation of hexadentate coordination complex from successive metal ion and a bidentate ligand:

$$M + L \leftrightarrows ML \qquad K_1 = \frac{\{ML\}}{[M][L]}$$

$$M + 2L \leftrightharpoons ML_2 \qquad K_2 = \frac{\{ML_2\]}{[ML][L]}$$

$$M + 3L \leftrightharpoons ML_3 \qquad K_3 = \frac{\{ML_3\]}{[ML_2][L]}$$

where K_1, K_2 and K_3 are the equilibrium constants and these are also called stepwise stability constants. The reciprocal $1/K_n$ is also used and referred as an instability constant.

A cumulative or overall constant, given the symbol β, is the constant for the formation of a complex from reagents. For example, the cumulative constant for the formation of ML_2 is given by:

$$M + 3L \leftrightharpoons ML_3 \qquad K_3 = \frac{\{ML_3\]}{[M][L]^3}$$
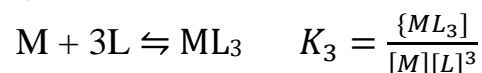
In this paper we describe results of evaluation of the stability of Fe(II) bipyridine complexes using a spectrophotometric method.

Experimetal

All reagents used in a current study was analytical pure grade and used without further purification. Stock solution preparation:

a) Fe(II) salts aqueous solutions prepared using 0.0345 g of FeSO$_4$·7H$_2$O dissolving in distilled water and 0,.0005M 250 mL solution obtained.

b) In order to prepare bipyridine (C$_{10}$H$_8$N$_2$) solution 0.0195 g of reagent weighed and dissolved in ethanol and consequently diluted with distilled water until to get 250 mL volume.

To get different complexes, total 10 mL of reagent mixture was used. The following table describes the used series:

Table 1.

Compostion of series of solutions for the experiments/

№	1	2	3	4	5	6	7	8	9	10	11
FeSO$_4$·7H$_2$O	10,00	9,00	8,00	7,00	6,00	5,00	4,00	3,00	2,00	1,00	0,00
C$_{10}$H$_8$N$_2$	0,00	1,00	2,00	3,00	4,00	5,00	6,00	7,00	8,00	9,00	10,00

Obtained solutions were mixed thoroughly until the reaction has finished. UV-2600i Shimadzu UV-vis double beam spectrophotometer was used during the study. Absorbence measurements on $\lambda_{max} = 522$ nm.

Fe(II) mole fraction was started from vthe very high to the low. All measurements were repeted 3 times and average valuse were used prior to calculaitio.

Results and discussion

As mentioned before $[Fe(bpy)_n]^{2+}$ complex has a disntict peak at 522 nm (Figure 1). The absorbance values of solutions can be seen in Table 2.

Table 1.

Absorbance values of Fe(II) complexes with different ration of bipyridine ligands

№	Mole fraction of Fe^{2+}	Absorbance (a.u.)
1	1	0.00
2	0.9	0.15
3	0.8	0.251
4	0.7	0.379
5	0.6	0.54
6	0.5	0.664
7	0.4	0.795
8	0.3	0.927
9	0.216	1.047
10	0.2	0.963
11	0.1	0.507
12	0	0.01

There is a similarity between a Jobs plot and a titration. In a typical Job's plot the total volume is kept constant in order to keep the reactant and product concentrations upon dilution. Thus in a Job's plot each measurement is a unique solution where the mole fraction of reactants are varied. As can be seen from the Table 2, complex containing 0.216 mole fraction of Fe(II) and 0.784 mole fraction bipyridine shows the highest absorbance. This value corresponds the coordination complex of $[Fe(bpy)_3]^{2+}$ - *tris*(bipyridine)iron(II).
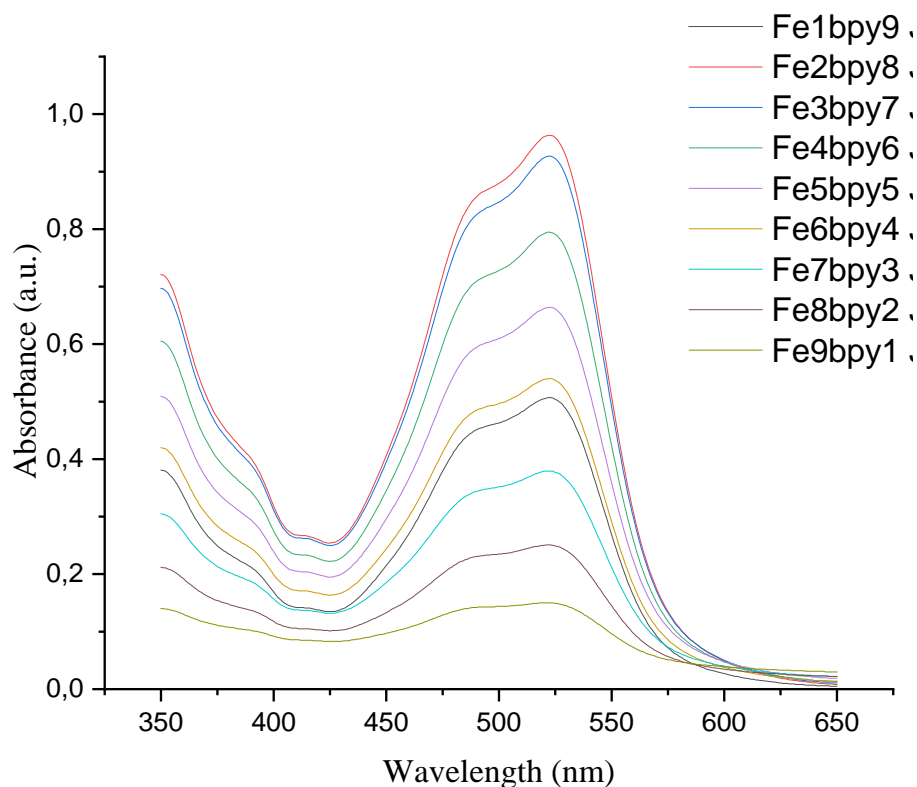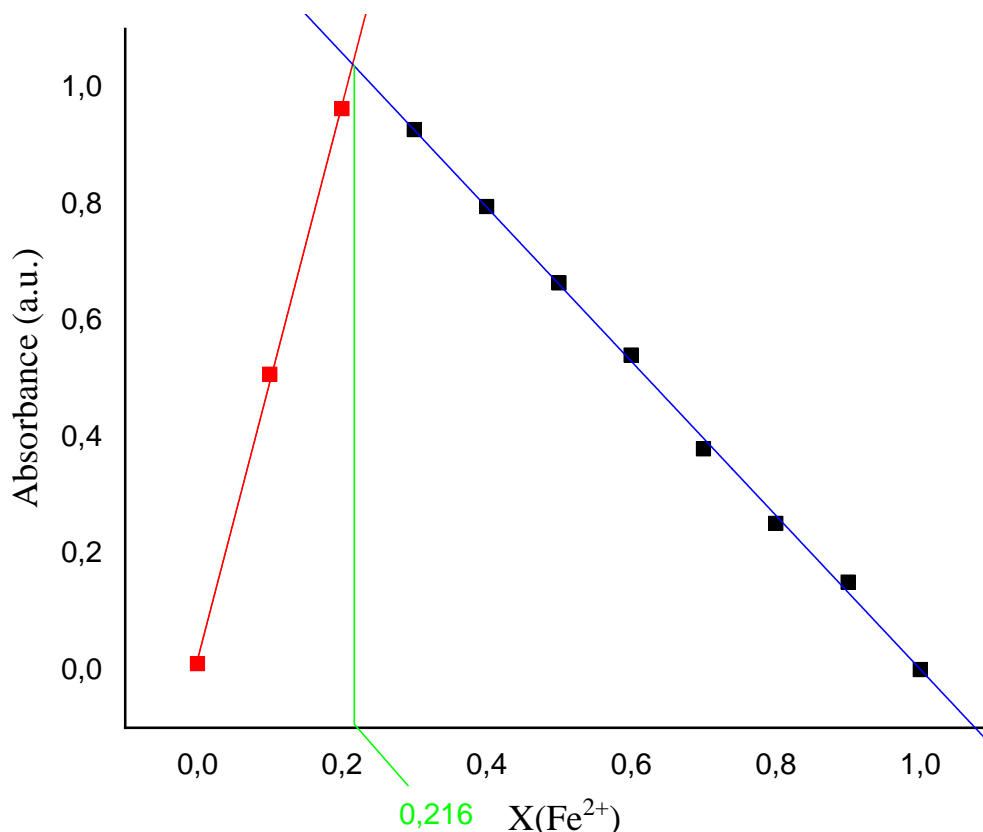
Figure 1. UV-vis spectra of the prepared coordination complex solutions.

The crystal field splitting energy for Fe(bpy)$_3$]$^{2+}$ - can be estimated using the famous Planck's equation:

$$\Delta_O = \frac{h \cdot c}{\lambda} N_A = \frac{6{,}626 \cdot 10^{-34} \text{ J} \cdot \text{s} \cdot 2{,}998 \cdot 10^8 \frac{\text{m}}{\text{s}}}{522 \cdot 10^{-9} \text{ m}} \cdot 6{,}02 \cdot 10^{23} \text{ mol}^{-1} = 229 \frac{\text{kJ}}{\text{mol}}$$

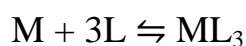Figure 2 depicts the Job's plot obtained using the commercial software.

The following calculations were used to get the final results:

$$A_{real} = 1.047$$

$$A_{max} = 4.785 \cdot (0.216) + 1.683 \cdot 10^{-2} = 1.05$$

$$C_{max} = 0.216 \cdot 0.0005 = 1.08 \cdot 10^{-4}$$

$$C_{real} = C_{max} \frac{A_{real}}{A_{max}} = 1.077 \cdot 10^{-4}$$

$$M + 3L \leftrightharpoons ML_3$$

$$K_f = \frac{[ML_3]}{[M][L]^3}$$

Reactants	**M**	**3L**	**ML₃**
Initial	$1.08 \cdot 10^{-4}$	$0.65 \cdot (0.0005)$	0
Change	$1.077 \cdot 10^{-4}$	$3 \cdot 1.077 \cdot 10^{-4}$	$1.077 \cdot 10^{-4}$
Equilibrium	$0.003 \cdot 10^{-4}$	$0.23 \cdot 10^{-4}$	$1.077 \cdot 10^{-4}$

$$K_f = \frac{1.077 \cdot 10^{-4}}{0.003 \cdot 10^{-4}(0.23 \cdot 10^{-4})^3} = 2.95 \cdot 10^{16}$$

Conclusions

Overall stability constants of bipyridine complex of Fe(II) in aqueous media was determined. Job's methods was utilized to evaluate the desired value. Crystal field splitting energy was also estimated.

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