

DETERMINATION OF THE BINDING CONSTANT OF TRIS-(3, 4, 7, 8- TETRAMETHYL-1, 10-PHENANTHROLINE) IRON (II) SULPHATE WITH SODIUM DODECYL SULPHATE

LATONA D. F¹, SORIYAN O. O² & IGE J³

¹Landmark University, Department of Physical Sciences, PMB, Omu-Aran, Nigeria

^{2,3}Obafemi Awolowo University, Department of Chemistry, Ile-Ife, Nigeria

ABSTRACT

The binding of tris- 3,4,7,8 – tetramethyl- 1,10- phenanthroline)iron(II) sulphate with sodium dodecyl sulphate was done using a unicam UV-Visible spectrophotometer at 25°C and the analyses were done by employing double reciprocal plots. Absorbance were taken at fixed concentration of the metal complex ($1.45 \times 10^{-5} \text{ mol dm}^{-3}$) and the concentration range of sodium dodecyl sulphate was far below the critical micelle concentration of the surfactant (2.00×10^{-5} - $3.50 \times 10^{-4} \text{ mol dm}^{-3}$). The binding study was done as a function of alkaline, acidic, benzoate ion and urea concentration at fixed concentration range of 0.50×10^{-5} – $3.00 \times 10^{-5} \text{ mol dm}^{-3}$. Binding increased at low $[\text{H}^+]$ to reach a maximum at $[\text{H}^+] = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$ after which there was a decrease in binding. The binding reaction was retarded in the presence of OH^- and urea and enhanced in benzoate ion.

KEYWORDS: Sulphate with, Sodium Dodecyl Sulphate, Li (32.2 M^{-1}), Na (36.9 M^{-1}), K (52.6 M^{-1}), Rb (55.9 M^{-1}) and Cs (54.0 M^{-1})

INTRODUCTION

Binding constant otherwise known as equilibrium constant is a ratio of rate constant of association and dissociation in binding studies. Over the years a lot of researches have been reported on binding constant determination using various techniques.

The equilibrium binding constants of Group I metal cations with gramicidin A in aqueous dispersion of lyso-pc have been determined employing a combination of competitive binding with the Tl^+ ion and Tl^+ - 205 NMR spectroscopy (Hinton et al., 1986). The binding constants at 34°C of the Group I metals were reported as Li (32.2 M^{-1}), Na (36.9 M^{-1}), K (52.6 M^{-1}), Rb (55.9 M^{-1}) and Cs (54.0 M^{-1}). While the equilibrium binding constant for the Tl^+ ion at this temperature was reported as 582 M^{-1} . The relationship between the binding constants, free energy of the binding process, and the cation selectivity of the gramicidin A channel were discussed.

Furthermore, on Alkali metal ions, the binding constants between polymer-supported azacrown ether ion exchanger, {(4,5) : (13,14) – dibenzo- 6,9,12 – trioxa – 3,15, 21- triazabicyclo[15.3.1] heneicosa – 1(21), 17,19 - triene-2,16- dione: DBPDA ion exchanger} with alkali metal ions (Li^+ , Na^+ , K^+) picrates were studied by spectrophotometry. The binding constants of alkali metal ions were in the order $\text{Li} < \text{Na} < \text{K}$ and that the alkaline metal ions formed 1:1 complexes with ligands of DBPDA ion exchanger. The enthalpy and entropy changes were found in the ranges of -2.71 – 3.79 kcal/mol and -16.52 - 20.57 eu , respectively (Choi et al., 1993). Binding constants between Indomethacin Ester to Human serum Albumin were calculated by Scatchard model. It was reported that the binding to human serum albumin was $14 \times 10^{-5} \text{ mol/l}$ (Trnavska and Verner, 1983).

Moreover, the kinetics and equilibrium binding of dyes, 2 – (p- Toluidino) naphthalene-6-sulfonate (TNS) and N- (4 – sulfobutyl)- 4- [4 – [p- (dipentylamino) phenyl] butadienyl} pyridinium inert salt (RH421) to ribulose 1, 5 – bisphosphate carboxylase/ oxygenase (RUBISCO) was investigated. The investigation revealed that TNS binds in a reversible bimolecular reaction non – covalently to RUBISCO, the water – soluble enzyme for carbon dioxide fixation and that TNS dose not change the substrate activity at the active site of RUBISCO. The rate constants for the association and dissociation were given as $(1.2 \pm 0.2) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1020 \pm 300 \text{ s}^{-1}$, respectively. While the binding of RH421 to RUBISCO was reported to be a diffusion – controlled reversible bimolecular reaction with an association rate constant of $(7 \pm 0.6) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and dissociation rate constant of $(1.8 \pm 0.2) \times 10^4 \text{ s}^{-1}$. The dissociation constants obtained from kinetically determined rate constants were in good agreement with those measured by equilibrium techniques (Frank et al., 1997).

The association of Rose Bengal (RB) with bovine serum albumin (BSA) was investigated by absorption spectroscopy and the binding constant was determined from the effect observed in the absorbance at 548nm upon addition of the protein according to the Benesi – Hildebrand treatment. It was concluded that the RB to BSA interaction was dominated by hydrophobic effects (Abuin et al., 2007).

MATERIALS AND METHODS

Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) sulphate, $\text{Fe}(\text{Me}_4\text{phen})_3\text{SO}_4$ was synthesized and purified according to the literature method (Shakhashuri, and Gordon, 1964). The complex was characterized by its UV-visible spectra. The maximum absorption peaks (λ_{max}) determined was 500nm. These are in excellent agreement with the literature values (Shakhashuri and Gordon, 1964)

Purified sodium dodecyl sulphate (99%) was used without further recrystallisation. The purity was ascertained by determination of the critical micelle concentration inaqueous solution at 25°C. The value of $8.20 \times 10^{-3} \text{ mol dm}^{-3}$ obtained is in good agreement with the literature value (Williams et al, 1985). Analar grade (BDH) sodium hydroxide (NaOH), sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$), sulphuric acid (H_2SO_4), and urea were used.

Synthesis of Tris-(3, 4, 7, 8-Tetramethyl-1, 10-Phenanthroline) Iron (II) Sulphate

Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) sulphate was synthesized by dissolving a mixture of 0.3985 g ($\approx 1.686 \times 10^{-3}$ mole) of 3, 4, 7,8 tetramethyl (1, 10-phenanthroline) ligand and 0.2204 g ($\approx 5.621 \times 10^{-4}$ mole) of ferrous ammonium sulphate ($\text{FeSO}_4(\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$) in 5 ml of distilled water in a beaker. The resulting dark red solution was heated .Then the solution was stirred briefly and allowed to cool at room temperature. It was later left to dry in a dessicator.

Investigation of Binding of Iron (II) Complexes with Sodium Dodecyl Sulphate (SDS)

The investigation of binding of Iron (II) complexes with sodium dodecyl sulphate (SDS) was done using a Unicam UV-Visible spectrophotometer and the analysis were done using double reciprocal plot. The absorbance was taken at maximum absorption peak (λ_{max}) and the concentration range of sodium dodecyl sulphate was $(2.00 \times 10^{-5} - 3.50 \times 10^{-4} \text{ mol dm}^{-3})$. The fraction of Iron (II) complex ion bound (α) to the SDS was calculated from:

$$\alpha = \frac{A - A_0}{A_\infty - A_0}$$

Where A_0 = absorbance of the complex when no SDS was added

A_∞ = absorbance when the Iron (II) complex solution was saturated with SDS.

A = absorbance when known amounts of SDS were added. Concentration of total Iron (II) complex ion, was obtained by using the molar extinction coefficient at λ_{max} . The concentration of the free Iron(II) complex ion $[Fe^{2+}]_f$ was obtained from

$$[Fe^{2+}]_f = [Fe^{2+}]_T - \alpha [Fe^{2+}]_T$$

where $[Fe^{2+}]_T$ is the total concentration of Iron (II) complex. The average number of molecules of iron (II) complex combined with each SDS (ν) was obtained from:

$$\nu = \frac{[Fe^{2+}]_{bound}}{[SDS]_{Total}}$$

The plot of $1/\nu$ against $1/[Fe^{2+}]_f$ was made and the binding constants, were calculated from the slope and intercept using the below equation:

$$\frac{1}{\nu} = \frac{1}{n_s} + \frac{1}{n_s K [Fe^{2+}]_f}$$

RESULTS AND DISCUSSIONS

The binding constants were obtained from double reciprocal plot as shown in Figure 1. The binding constant of tris- 3,4,7,8- tetramethyl- (1,10- phenanthroline)iron(II) sulphate, $Fe(Me_4phen)_3^{2+}$ with sodium dodecyl sulphate, SDS in neutral medium was 3.94×10^5 . At fixed concentration range of acid, binding increased to a maximum value and later decreased with increase in $[H^+]$. Maximum was at $[H^+] = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$. Table 1 shows the binding constants (K) as a function of $[H^+]$ in $Fe (Me_4phen)_3^{2+}$. Increase in binding constant with increase in $[H^+]$ was due to the dominance of hydrophobic interaction at low acid concentrations which allows rapid attraction of the complex to the pre micellar surface due to higher negative charge density on SDS. However, as protonation of SDS increases there was consequent decrease in the negative charge density on the pre micelles thereby leading to a decrease in binding. This is in consonance with the kinetic data.

The effect of added sodium benzoate on the binding constant revealed general increase in binding constants with increase in benzoate ion concentrations Table 2. The reason for the increase is due to the orientation of the phenyl group on the benzoate ion which aligns itself below the head groups of SDS monomers via hydrophobic interaction causing an increase in the negative charge density in the region of the head group and therefore leading to increased coulombic attraction between the metal complex and the monomers.

Furthermore, at fixed concentration range of hydroxyl ion ($5.00 \times 10^{-6} - 3.00 \times 10^{-5} \text{ mol dm}^{-3}$). Binding constant as a function of OH^- showed that binding constant decreased with increase in $[OH^-]$ as shown in Table 3. The reason is that OH^- increases the dielectric constant of the medium of the reaction, hence leading to a decrease in the hydrophobicity of the medium. Therefore, hydrophobic interaction between the metal chelate complex and SDS was reduced. Binding constant decreased with increased in [urea] as evident in Table 4. This is attributed to the fact that urea reduces the

negative charge density on SDS which consequently led to a decrease in electrostatic attraction between the metal center of the metal complex and SDS.

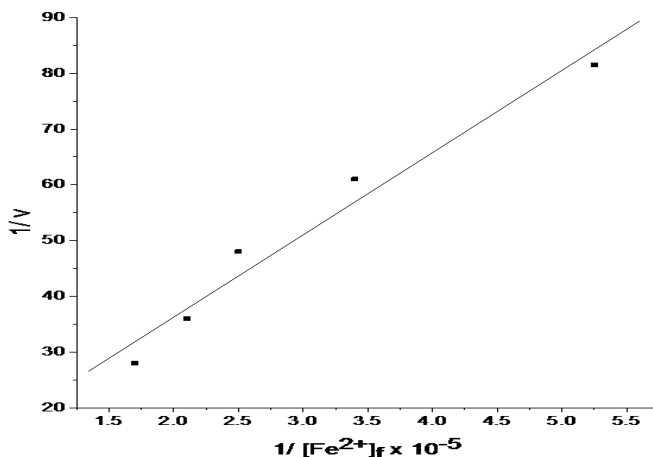


Figure 1: Plot of $1/v$ versus $1/[Fe^{2+}]_f$ as a Function of $0.50 \times 10^{-4} \text{ mol dm}^{-3} \text{ H}^+$ of Binding between $Fe(Me_4phen)_3^{2+}$ and SDS

Table 1: Binding Constant (K) as a Function of $[H^+]$

	$[Fe(Me_4phen)_3^{2+}] = 1.45 \times 10^{-5} \text{ mol dm}^{-3}$
$[H^+] \text{ mol dm}^{-3}$	$K \pm 1.35 \times 10^4$
0.50×10^{-4}	2.58×10^4
1.00×10^{-4}	2.99×10^4
1.50×10^{-4}	5.21×10^4
2.00×10^{-4}	6.16×10^4
2.50×10^{-4}	5.39×10^4
3.00×10^{-4}	5.28×10^4

Table 2: Binding Constant (K) as a Function of $[C_6H_5COONa]$

	$[Fe(Me_4Phen)_3^{2+}] = 1.45 \times 10^{-5} \text{ mol dm}^{-3}$
$[C_6H_5COONa] \text{ mol dm}^{-3}$	$K \pm 1.02 \times 10^5$
0.50×10^{-5}	1.54×10^5
1.00×10^{-5}	1.74×10^5
1.50×10^{-5}	1.77×10^5
2.00×10^{-5}	2.01×10^5
2.50×10^{-5}	2.08×10^5
3.00×10^{-5}	4.27×10^5

Table 3: Binding Constant (K) as a Function of $[OH^-]$

	$[Fe(Me_4Phen)_3^{2+}] = 1.45 \times 10^{-5} \text{ mol dm}^{-3}$
$[OH^-] \text{ mol dm}^{-3}$	$K \pm 0.16 \times 10^5$
0.50×10^{-5}	1.54×10^5
1.00×10^{-5}	1.36×10^5
1.50×10^{-5}	1.34×10^5
2.00×10^{-5}	1.21×10^5
2.50×10^{-5}	1.15×10^5
3.00×10^{-5}	1.10×10^5

Table 4: Binding Constant (K) as a Function of [Urea]

[urea] mol dm ⁻³	[Fe(Me ₄ Phen) ₃ ²⁺]=1.45 x 10 ⁻⁵ mol dm ⁻³ K ± 0.14 x 10 ⁵
0.50 x 10 ⁻⁵	1.56 x 10 ⁵
1.00 x 10 ⁻⁵	1.39 x 10 ⁵
1.50 x 10 ⁻⁵	1.28 x 10 ⁵
2.00 x 10 ⁻⁵	1.25 x 10 ⁵
2.50 x 10 ⁻⁵	1.20 x 10 ⁵
3.00 x 10 ⁻⁵	1.18 x 10 ⁵

CONCLUSIONS

The binding constant is majorly dependent on the rate constant of association than rate constant of dissociation. Results obtained from earlier work on the kinetics of binding of association reaction followed the same trend with the binding constant determination for the same reaction. Generally, rate constants of association is far greater than that of dissociation. The greater the binding constant the lower the rate of dissociation and vice – versa or the more stabilized the complex is with respect to dissociation. The binding process is best explained by both hydrophobic/electrostatic attraction between the metal complex and the surfactant as both phenomenon was used to explain the results obtained. However, in the absence of the substrates, hydrophobic effect took precedence over electrostatic attraction. Conversely, in the presence of substrates like H⁺, OH⁻, C₆H₅COO⁻ and urea, electrostatic effect best explain the binding reaction.

REFERENCES

1. Abuin A, Aspee A, Lissi E, Leon L. (2007). Binding of rose bengal to bovine serum albumin. *J. Chil. Chem. Soc.* 52, No 2, 1196– 1197.
2. Choi Y. K, Kim D.W, Kim C.S and Jeon Y.S. (1993). Binding properties of Alkali Metal ions with DBPDA ion exchanger. *Journal of the Korean chemical society*, vol. 37, No. 5, 12 – 16.
3. Frank J, Holzwarth J.F, VanHoek A, Vissei J.W.G and Vater J. (1997). Kinetics and equilibrium binding of the dyes TNS and RH421 to ribulose 1, 5 –bisphosphate carboxylase / oxygenase(RUBISCO). *J. Chem. Soc., Faraday Trans.*, 2379 – 2385.
4. Hinton J.F, Whaley W.L, Shungu D, Koeppe R.E and Millett F.S (1986). Equilibrium binding constants for the group I metal with gramicidine – A determined by competition studies Tl⁺ 205 nuclear magnetic resonance spectroscopy. *Biophys. J.*; 50(3); 539 – 544.
5. Trnavska Z, Verner P (1983). Binding of Indomethacin Ester with Tropic Acid to Human Serum Albumin. *Pharmacology* vol. 26, No. 5, 270 – 273.
6. Shakhashuri B.Z and Gordon G. (1964). The oxidation of tris-(1, 10- phenanthroline) iron (II) by aqueous chloride. *Inorg. Chem.*7, 2454 – 2456.
7. Williams R.J, Phillips J.W and Mysel K.J. (1985). Critical micelle concentration of sodium dodecyl sulphate at 25oC. *Trans. Faraday Soc.* 51, 728- 737.

