IMPACT: International Journal of Research in Applied, Natural and Social Sciences (IMPACT: IJRANSS)
ISSN(E): 2321-8851; ISSN(P): 2347-4580
Vol. 2, Issue 5, May 2014, 153-156

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

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ABSTRACT

The binding constants were carried out using a unicam UV- Visible spectrophotometer at 25^{o}C and data were analysed by double reciprocal plots. Absorbances were taken at fixed concentration of the metal complex (1.80 x 10^{-5} mol dm^{-3}) and the concentration of sodium dodecyl sulphate (SDS) was far less than the critical micelle concentration. The binding study was also carried out in alkaline, acidic, benzoate ion and urea at fixed concentration range, 5.00 x 10^{-6} – 3.00 x 10^{-5} mol dm^{-3}. Binding between tris-4,7- dimethyl (1,10 – phenanthroline) perclorate and sodium dodecyl sulphate was accelerated at low [H^{+}] until a maximum at [H^{+}] = 1.00 x 10^{-4} mol dm^{-3} before it started to decrease at higher acid concentrations. However, the binding process was enhanced in the presence of hydroxyl ion, benzoate ion and urea.

KEYWORDS: Sodium Hydroxide (NaOH), Sodium Benzoate (C_6H_5COONa), Sulphuric Acid (H_2SO_4)

INTRODUCTION

A lot of research work has been reported on binding studies among which includes the report on the thermodynamics and kinetics of D- ribulose 1,5- biphosphate (RuBP) and effector 6-D-phosphogluconate (6-PG) binding to D- ribulose 1,5- biphosphate carboxylase / oxygenase (RUBISCO) from spinach by micro calorimetric and fast reaction techniques. Dissociation constant kd and enthalpy change ΔH_b associated with the strong binding of RuBP to RUBISCO were measured by isothermal differential titration calorimetry (Frank et al., 1988). The kinetics of the binding of Zinc(II) by bovine apocarbonic anhydrase is accompanied by the liberation of protons and by small changes of absorptivity in the ultraviolet spectrum. Neutral salts and pH increase accelerated the reaction (Henkens and Sturtevant, 1968). Furthermore, crystallographic and kinetic study of cyanide binding to Truncated Hemoglobins at pH 7.0 and 20^{o}C revealed that complexes formed are very stable and values of the association equilibrium constant was higher than 10^{5} M^{-1} and values of the first- order dissociation rate constant ranged between 1 x 10^{-2} and 1 x 10-6 s^{-1} (Milani et al., 2004).

The kinetics of the binding of cyanide by enzyme ferric bovine lactoperoxidase at 25^{o}C by means of temperature – jump technique showed that the association rate data is pH dependent due to the presence of two ionizable groups in the active site of the enzyme (Dolman et al., 1968). Concentration dependence of the observed rate of Caldesmon-actin binding was analysed to a first approximation as a single- step reaction using a Monte Carlo simulation in the the study of the kinetics of binding of 12- (N- methyl-N- (7- nitrobenzene- 2-oxa 1,3 – diazol-4- yl) labeled Caldesmon to actin. The derived association and dissociation constants were 10^{7} $M^{-1}S^{-1}$ and 18.2 S^{-1} respectively (Chalovich et al., 1995).

MATERIALS AND METHODS

Tris-(4,7- dimethyl-1,10-phenanthroline) iron (II) perchlorate, $[Fe(Me_2phen)_3]$ $(ClO_4)_2$ were 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 (λmax) determined was 510nm for Tris- (4,7dimethyl –1, 10 – phenanthroline) iron (II) perchlorate. This is 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 in aqueous solution at 25°C. The value of 8.20 x 10^{-3} mol dm^{-3} obtained is in good agreement with the literature value (Williams et al, 1985).

Analar grade (BDH) sodium hydroxide (NaOH), sodium benzoate (C_6H_5COONa), sulphuric acid (H_2SO_4) and urea were used.

Synthesis of Tris-(4,7- Dimethyl-1,10-Phenanthroline) Iron (II) Perchlorate

Tris – (4,7 dimethyl – 1,10 – phenanthroline) iron (II) perchlorate was synthesized by dissolving 0.354 g (1.686 x 10^{-3} mole) of 4,7 dimethyl – 1,10 –phenanthroline) ligand and 0.204 g (5.621 x 10^{-4} mole) of ferrous perchlorate $(Fe(ClO_4)_2.6H_2O$ in 5 ml of distilled water in a beaker. The resulting dark red solution was heated to just below boiling point. The solution was stirred briefly and allowed to cool at room temperature. It was later left to dry in the 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 (λmax) and the concentration range of sodium dodecyl sulphate was (2.00xl0^{-5} - 3.50 xl0^{-4} mol dm^{-3}). The fraction of Iron(II) complex ion bound (α) to the SDS was calculated from:

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

Where Ao = 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 (υ) was obtained from:

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

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

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

RESULTS AND DISCUSSIONS

The binding constant of tris- 4,7 dimethyl- (1,10- phenanthroline) Iron (II) perchlorate, $Fe(Me_2phen)_3^{2+}$, with sodium dodecyl sulphate, SDS in neutral medium was 1.41 x 10^6. Binding increased at fixed acid concentration range to a maximum at $[H^+]$ = 1.00 x 10^{-4} mol dm^{-3} and consequently decreased with increase in acid concentration. Table 1 shows the binding constants as a function of $[H^+]$ in $Fe(Me_2phen)_3^{2+}$ complex. Reason for the rise and fall of binding constant with respect to $[H^+]$ is due to the dominance of hydrophobic interaction at low acid concentrations which promotes hydrophobic attraction of the complex to the premicellar 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 premicelles hence leading to decrease in binding.

The effect of added sodium benzoate on the binding constant showed general increase in binding constants with increase in benzoate ion concentration (Table 2). This is because of the orientation of the phenyl group of the benzoate ion which aligns itself below the head groups of SDS monomers via hydrophobic interaction leading to an increase in the negative charge density in the region of the head group and thereby causing an increase in the electrostatic attraction between the metal centre and the surfactant monomers. Binding constant as a function of OH^- increased with increase in $[OH^-]$ as depicted in Table 3. This is due to the formation of a complex anion as a result of polymerization between ClO_4^- and OH^- in solution which increased the negative charge density on SDS, thereby leading to electrostatic interaction between $Fe(Me_2phen)_3^{2+}$ and SDS. Furthermore, increase in the binding constant as a function of urea (Table 4) was attributed to the removal of urea by ClO_4^-, forming urea perchlorate in solution which consequently led to electrostatic and hydrophobic interactions between $Fe(Me_2phen)_3^{2+}$ and SDS.

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

$[H^+]$ mol dm^{-3}	$[Fe(Me_2phen)_3^{2+}]$=1.80 x 10^{-5} mol dm^{-3} K ± 2.18 x 10^5
0.50 x 10^{-4}	7.58 x 10^5
1.00 x 10^{-4}	9.50 x 10^5
1.50 x 10^{-4}	5.55 x 10^5
2.00 x 10^{-4}	5.48 x 10^5
2.50 x 10^{-4}	4.18 x 10^5
3.00 x 10^{-4}	3.69 x 10^5

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

$[C_6H_5COONa]$ mol dm^{-3}	$[Fe(Me_2phen)_3^{2+}]$=1.80 x 10^{-5} mol dm^{-3} K ± 0.22 x 10^6
0.50 x 10^{-5}	2.11 x 10^6
1.00 x 10^{-5}	2.16 x 10^6
1.50 x 10^{-5}	2.24 x 10^6
2.00 x 10^{-5}	2.30 x 10^6
2.50 x 10^{-5}	2.50 x 10^6
3.00 x 10^{-5}	2.69 x 10^6

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

[OH^-] mol dm^{-3}	$[Fe(Me_2phen)_3^{2+}]=1.80 \times 10^{-5}$ mol dm^{-3}
	$K \pm 0.41 \times 10^6$
0.50×10^{-5}	1.45×10^6
1.00×10^{-5}	1.68×10^6
1.50×10^{-5}	1.78×10^6
2.00×10^{-5}	2.14×10^6
2.50×10^{-5}	2.30×10^6
3.00×10^{-5}	2.54×10^6

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

[Urea] mol dm^{-3}	$[Fe(Me_2phen)_3^{2+}]=1.80 \times 10^{-5}$ mol dm^{-3}
	$K \pm 2.05 \times 10^5$
0.50×10^{-5}	8.52×10^5
1.00×10^{-5}	8.61×10^5
1.50×10^{-5}	9.45×10^5
2.00×10^{-5}	1.22×10^6
2.50×10^{-5}	1.24×10^6
3.00×10^{-5}	1.30×10^6

CONCLUSIONS

The binding of an association complex of anion surfactant with Fe(II) chelate in aqueous surfaces suggest that hydrophobic /electrostatic interactions plays an important role in the formation of ion- pair between the complex and sodium dodecyl sulphate. Hydrophobic interaction best explain the binding process in the absence of substrates. Conversely, in the presence of substrates like H^+, OH^-, $C_6H_5COO^-$ and urea, electrostatic effect best explain the binding reaction.

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