ISSN: 2716-9227 Algerian Journal of Engineering and Technology 05 (2021) 038–042 e-ISSN: 2716-9278

Algerian Journal of Engineering and Technology

Journal homepage: https://jetjournal.org/index.php/ajet

Original Article

Equilibrium binding constants of Tris-(3,4,7,8-Tetramethyl-1,10-phenanthroline)Iron(II) Sulphate and Tris-(4,7- dimethyl-1,10-phenanthroline)Iron(II) Perchlorate with Sodium Dodecyl Sulphate. A comparative study

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ARTICLE INFO

Article history:
Received 05 May 2021
Revised 07 July 2021
Accepted 10 October 2021

Keywords:
Tris-(3,4,7,8-Tetramethyl-1,10-phenanthroline)Iron(II) Sulphate ($Fe(Me_4phen)_3^{2+}$);
Tris-(4,7- dimethyl-1,10-phenanthroline)Iron(II) Perchlorate($Fe(Me_2phen)_3^{2+}$);
Sodium Dodecyl Sulphate (SDS);
Equilibrium binding constants.

ABSTRACT

Binding constants were investigated with a double beam unicam UV-Visible spectrophotometer at maximum absorption peaks (λmax) of 500nm and 510 nm for tris–(3,4,7,8 – tetramethyl -1,10- phenanthroline)iron(II) sulphate and Tris- (4,7-dimethyl –1,10 – phenanthroline)iron(II) perchlorate, respectively and the data were analyzed using double reciprocal plots. Absorbances were taken at fixed concentration of the metal complexes and the concentrations of sodium dodecyl sulphate (SDS) were far less than the critical micelle concentration (CMC). The effect of alkaline, acid, benzoate ion and urea on binding constants were investigated. Binding between Tris-(4,7-dimethyl-1,10-phenanthroline)Iron(II) Perchlorate($Fe(Me_2phen)_3^{2+}$ and Sodium dodecyl sulphate was accelerated at low $[H^+] = 1.00 \times 10^{-4}$ mol dm^{-3} and decreased at higher acid concentrations. However, binding was enhanced in the presence of hydroxyl ion, benzoate ion and urea. Furthermore, binding between Tris-(3,4,7,8-Tetramethyl-1,10-phenanthroline)Iron(II) Sulphate and sodium dodecyl sulphate was accelerated at low$[H^+] = 1.00 \times 10^{-4}$ mol dm^{-3} to reach a maximum at $[H^+] = 2.00 \times x\ 10^{-4}$ mol dm^{-3} after which it decreased at higher acid concentrations. However, binding was retarded in the presence of hydroxyl ion and urea but enhanced in benzoate ion.

1. Introduction

The equilibrium binding constants of Group I metal cations with gramicidin A in aqueous dispersion of lyso-PC have been determined by employing a combination of competitive binding with the Tl+ ion and Tl-205 NMR spectroscopy [1]. Furthermore, the binding constants between polymer-supported aza crown ether ion exchanger with alkali metal ions were studied by spectrophotometry. The binding constants of alkali metal ions were in the order Li<Na<K and that the alkaline metal ions formed 1:1 complexes with ligands DBPDA ion exchanger [2]. Binding constants between Ester of indomethacin to human serum albumin were calculated by Scatchard model [3]. Moreover, the kinetics and equilibrium binding of dyes, 2-(p-Toludino) 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 study showed that TNS binds in a reversible bimolecular reaction non-covalently to RUBISCO, the water-soluble enzyme for carbon dioxide fixation and that TNS does not change the substrate activity at the active site of RUBISCO [4].

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Peer review under responsibility of University of Echahid Hamma Lakhdar.

http://dx.doi.org/ 10.5281/zenodo.5559632

The association of Rose Benga l(RB) with bovine serium 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 effect [5]. Binding constants of reactions have been determined by employing electron spray ionization mass spectrometry [6], Algorithm [7] and NMR[8,9].

2. Materials and Methods

Analar grade (BDH) sodium hydroxide (NaOH), sodium benzoate (C_6H_5COONa), sulphuric acid (H_2SO_4) and urea were used. Tris-(3,4,7,8-tetramethyl-l,10-phenanthroline)iron(II)sulphate, $[Fe(Me_4phen)_3]SO_4$ and 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 [10]. The complexes were characterized by their UV-visible spectra. The maximum absorption peaks (λmax) determined were 500nm and 510nm for tris – (3,4,7,8 –tetramethyl-1,10-phenanthroline)iron(II) sulphate and Tris- (4,7dimethyl–1,10–phenanthroline)iron(II)perchlorate, respectively. These are in excellent agreement with the literature values [10]

Purified sodium dodecyl sulphate (99%) was used without further re-crystallization. The purity was ascertained by determination of the critical micelle concentration in aqueous solution at 25°C. The value of 8.20×10^{-3} mol. L^{-1} obtained is in good agreement with the literature value [11].

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) of the complexes and the concentration range of sodium dodecyl sulphate was ($2.00 \times l0^{-5}$ - $3.50 \times l0^{-4}$ mol.L^{-1}). The fraction of Iron(II) complex ion bound (α) to the SDS was calculated from:

$$\propto = \frac{A - A_o}{A_\infty - A_O} \qquad (1)$$

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:

$$\upsilon = \frac{[Fe^{2+}]_{bound}}{[SDS]_{Total}} \qquad (2)$$

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:

$$\frac{1}{\upsilon} = \frac{1}{n_s} + \frac{1}{n_s K [Fe^{2+}]_f} \qquad (3)$$

This requires measurement of the absorbance of the complex at known concentrations of SDS below the critical micelle concentration (CMC). The binding study was done in neutral, alkaline and acidic media. In all the binding studies, the binding constant (K) were determined at 25°C by varying the concentrations of SDS from 2.00×10^{-5} to 3.50×10^{-4} mol.L^{-1} at fixed concentrations of $Fe(Me_4phen)_3^{2+}$ and $Fe(Me_2phen)_3^{2+}$ of 1.45×10^{-5} and 1.80×10^{-5} mol.L^{-1} respectively. The binding constants were calculated from the slope of the double reciprocal plots.

3. Results and Discussion

3.1. Binding of complex to SDS in neutral medium

The absorbance change with [SDS] increased non – linearly until saturation was reached at higher [SDS]. A typical plot of 1/υ against $1/[Fe^{2+}]_f$ is shown in Figure 1. The slopes gave calculated values of the binding constants for $Fe(Me_4phen)_3^{2+}$ and $Fe(Me_2phen)_3^{2+}$ as 3.94×10^5 and 1.41×10^6 respectively.

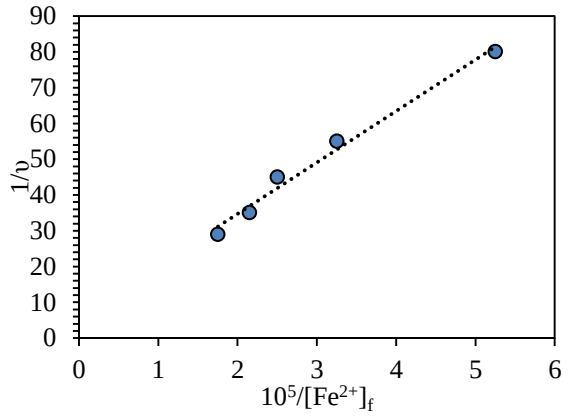

Fig 1. Plot of 1/v versus $1/[Fe^{2+}]_f$ as a function of 0.50 x 10^{-4} mol.L^{-1} $[H^+]$ for binding between $Fe(Me_4phen)_3^{2+}$ and SDS.

3.2. Effect of [H+] on binding constant

The fixed concentration range of acid was within 0.50 × 10^{-4} – 3.00 × 10^{-4} mol.L^{-1}. The results in Table 1 showed that for both complexes, binding constants increased to a maximum value and then decreased with $[H^+]$. The maximum for $Fe(Me_4phen)_3^{2+}$ complex was at $[H^+]$ equals 2.00 × 10^{-4} mol.L^{-1} and 1.00 × 10^{-4} mol.L^{-1} for $Fe(Me_2phen)_3^{2+}$. The corresponding values of the binding constants at these maxima are 6.20 × 10^4 and 9.50 × 10^5 for $Fe(Me_4phen)_3^{2+}$ and $Fe(Me_2phen)_3^{2+}$ respectively. Increase in binding constant was due to the dominance of hydrophobic interaction at low acid concentrations which allows rapid attraction of the complex to the premicellar surface due to higher negative charge density on SDS. However, as protonation of SDS increased there was consequent decrease in the negative charge density on the premicelles thereby leading to a decrease in binding. This was in consonance with the kinetic data.

Table 1. Binding Constant (K) as a function of $[H^+]$ in $Fe(Me_4phen)_3^{2+}$ and $Fe(Me_2phen)_3^{2+}$ Complexes.

	10^{-5}K	
$10^4[H^+]$/M	**$Fe(Me_4phen)_3^{2+}$**	**$Fe(Me_2phen)_3^{2+}$**
0.50	0.26	7.58
1.00	0.30	9.50
1.50	0.52	5.55
2.00	0.62	5.48
2.50	0.54	4.18
3.00	0.53	3.69

3.3. Effect of added sodium benzoate on the binding constant

The fixed concentration range of sodium benzoate was 0.50 × 10^{-5} – 3.00 × 10^{-5} mol.L^{-1}. The binding constants generally increased with increase in benzoate ion concentrations for both complexes as shown in Table 2. However, values are greater in $Fe(Me_2phen)_3^{2+}$ than in $Fe(Me_4phen)_3^{2+}$. The binding constant was higher for $Fe(Me_2phen)_3^{2+}$ than $Fe(Me_4phen)_3^{2+}$ by a factor of about 14 at each benzoate ion concentrations. The reason for the increase was due to the orientation of the phenyl group of 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 columbic attraction between the metal complex and the monomers.

Table 2. Binding Constant (K) as a function of $[C_6H_5COONa]$ in $Fe(Me_4phen)_3^{2+}$ and $Fe(Me_2phen)_3^{2+}$ Complexes.

	10^{-6}K	
$10^5[C_6H_5COONa]$/M	**$Fe(Me_4phen)_3^{2+}$**	**$Fe(Me_2phen)_3^{2+}$**
0.50	0.15	2.11
1.00	0.17	2.16
1.50	0.18	2.24
2.00	0.20	2.30
2.50	0.21	2.50
3.00	0.43	2.69

3.4. Effect of added [OH-] on the binding constant

The fixed concentration range of hydroxyl ion was within 0.50 × 10^{-5} – 3.00 × 10^{-5} mol.L^{-1}. The binding constant decreased with increase in $[OH^-]$ for the $Fe(Me_4phen)_3^{2+}$ but, increased with increase in $[OH^-]$ for $Fe(Me_2phen)_3^{2+}$ as shown in Table 3. Decrease in binding constant with increase in $[OH^-]$ is because increase in $[OH^-]$ increases the dielectric constant of the medium of reaction, hence leading to a decrease in the hydrophobicity of the medium. Therefore, hydrophobic interaction between the metal chelate complex and SDS was reduced. This was in agreement with kinetic data. However, increase in binding constant for $Fe(Me_2phen)_3^{2+}$ with SDS as a function of $[OH^-]$ was 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.

Table 3. Binding Constant (K) as a function of $[OH^-]$ in $Fe(Me_4phen)_3^{2+}$ and $Fe(Me_2phen)_3^{2+}$ Complexes.

	10^{-6}K	
$10^5[OH^-]$/M	$Fe(Me_4phen)_3^{2+}$	$Fe(Me_2phen)_3^{2+}$
0.50	0.15	1.45
1.00	0.14	1.66
1.50	0.13	1.78
2.00	0.12	2.14
2.50	0.11	2.30
3.00	0.10	2.54

3.5. Effect of urea on the binding constant

The fixed concentration of urea was in the range 0.50×10^{-5} – 3.00×10^{-5} $mol.L^{-1}$. The binding constant decreased with increase in [urea] for $Fe(Me_4phen)_3^{2+}$, but increased with increase in [urea] for $Fe(Me_2phen)_3^{2+}$. The binding constant was greater in $Fe(Me_2phen)_3^{2+}$ than in $Fe(Me_4phen)_3^{2+}$ as shown in Table 4 and the factor of increase was within the range 5.46 – 11.02. The reason was that urea reduces the negative charge density on SDS which leads to a decrease in the binding constant. However, increase in the binding constant for $Fe(Me_2phen)_3^{2+}$ with SDS as a function of urea was attributed to the removal of urea by ClO_4^- ion, forming urea perchlorate in solution which consequently led to electrostatic and hydrophobic interaction between $Fe(Me_2phen)_3^{2+}$ and SDS.

Table 4. Binding Constant (K) as a function of [Urea] in $Fe(Me_4phen)_3^{2+}$ and $Fe(Me_2phen)_3^{2+}$ Complexes.

	10^{-5}K	
10^5[Urea]/M	$Fe(Me_4phen)_3^{2+}$	$Fe(Me_2phen)_3^{2+}$
0.50	1.56	8.52
1.00	1.39	8.61
1.50	1.28	9.54
2.00	1.25	12.20
2.50	1.20	12.40
3.00	1.18	13.00

4. Conclusion

Binding constant is the ratio of the rate constant of binding/association and the rate constant of dissociation. Generally, rate of association is usually far greater than the rate of dissociation. In fact, the greater the binding constant the lower the rate of dissociation and vice-versa or in other words, the more stabilized is the complex with respect to dissociation. Therefore, hydrophobic/electrostatic interactions play major vital role in binding process.

Acknowledgements

The author wish to thank the authority of the Obafemi Awolowo University, Ile-Ife, Nigeria for the use of their state of the art facilities.

Conflict of Interest

There is no conflict of interest

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Recommended Citation
Latona DF. Equilibrium binding constants of Tris-(3,4,7,8-Tetramethyl-1,10-phenanthroline)Iron(II) Sulphate and Tris-(4,7- dimethyl-1,10-phenanthroline)Iron(II) Perchlorate with Sodium Dodecyl Sulphate. A Comparative Study. *Alger. J. Eng. Technol. 2021*, 5:38-42. http://dx.doi.org/ 10.5281/zenodo.5559632