The Kinetics of Binding of Tris-(3, 4, 7, 8-Tetramethyl-1, 10-Phenanthroline) Iron (II) Sulphate with Sodium DODECYL Sulphate

Latona D. F.¹, Ige W. J.² and Soriyan O. O.³

10sun State Polytechnic, Department of Applied Science, PMB 301, Iree, Nigeria. 2&3 Obafemi Awolowo University, Department of Chemistry, Ile-Ife, Nigeria.

ABSTRACT : The kinetics and effects of substrates on the binding of an anionic surfactant, sodium dodecyl sulphate (SDS) to tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II)sulphate (Fe(Me₄phen)₃²⁺ was investigated in this study. The kinetics of the reaction was studied by ultraviolet–visible (UV–VIS) spectrophotometry and the activation energy, Ea, free energy of

activation, ΔG^{\ddagger} , entropy of activation, ΔS^{\ddagger} and enthalpy of activation, ΔH^{\ddagger} were obtained from the temperature dependence study of the rate of binding using Eyring's equations.

The results showed that the reaction was invariant with Iron(II) complex concentration and that the rate of binding is inhibited by sodium dodecyl sulphate. The rate of binding was enhanced by H^+ at low $[H^+]$ and a maximum was reached at $[H^+]$ of 2.00 x $10^{-4}M$. Beyond these concentrations of H^+ , the reaction was inhibited by H^+ . The results further showed that hydroxyl ion and urea inhibited the binding of SDS to $Fe(Me_4phen)_3^{2+}$. The rate of binding was accelerated in the presence of benzoate ion. The effect of substrates on the activation energy were in the order: benzoate ion > H^+ > urea > OH >

Neutral. While negative values of ΔS^{\ddagger} in indicated that the formation of the activated complex from the reactants was

accompanied by a large decrease in entropy. Approximately the same values of ΔG^{\ddagger} were obtained suggesting a common *mechanism for the binding process.*

I. INTRODUCTION

1,10- phenanthroline ligand has wide application in Co-ordinate chemistry because of its ability to form stable chelates with transition metal. This ligand like other complexes of aromatic diimines has been greatly employed for the quantitative determination of metals (Alexiev et al., 1994). A study of DNA binding of Iron(II) complexes with 1,10-phenanthroline by spectrophotometric titration showed salt concentration dependence of the binding constant (Mudasir et al., 2003). Investigation on the catalysis of aquation of Iron(II) penanthroline complexes showed that the micellar inhibition was due to favourable thermodynamic/hydrophobic/electrostatic binding between the Fe(II) and sodium dodecyl sulphate monomer aggregates (Ige and Soriyan, 1986). Reports on the kinetic studies of racemisation and dissociation of Iron(II) phenanthroline complexes with sodium dodecyl sulphate revealed that racemisation and dissociation rates of the complexes increased with increase in sodium dodecyl sulphate concentration to reach limiting values at concentrations above the critical micelle concentration (Tachiyashiki and Yamatera, 1986). However, this work shall investigate the rate of binding of tris-(3,4,7,8-tetramethyl- 1,10-phenanthroline)iron(II) sulphate with sodium dodecyl sulphate in its monomeric form with the view to establishing quantitative insight into the extent of electrostatic and hydrophobic interaction between the complex and the anionic surfactant.

II. EXPERIMENTAL

The complex Fe(Me₄phen)₃SO₄ 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 peak (λ_{max}) determined was 500nm, which was in aggrement with the literature values (Shakhashuri and Gordon, 1964). Purified sodium dodecyl sulphate (99%) was used with further recrystallisation. The purity was ascertained by the determination of the critical micelle concentration (CMC) in aqueous solution at 25°C. The value of 8.20 x 10⁻³ mol dm⁻³ obtained was in good aggrement with the literature value (Williams et al., 1985). Analar grade (BDH), sodium hydroxide (NaOH), sodium benzoate (C₆H₅COONa), sulphuric acid (H₂SO₄) and urea were used.

II.1 Kinetics: Kinetic data were established by monitoring change in absorbance of ferrous complex at absorption maximum (λ max) as a function of time using unicam UV- visible spectrophotometer. The concentration of the complex was 1.45 x 10⁻⁵ mol dm⁻³. The concentration of sodium dodecyl sulphate ranged within (2.00 x 10⁻⁴ – 8.00 x 10⁻⁴ mol dm⁻³). The kinetic runs were performed under pseudo – first order kinetics and rates constants were obtained from the slope of In(A_∞ – A_t) versus time. The effect of H⁺, OH⁻, C₆H₅COONa and urea on binding were investigated. Activation parameters were determined within the temperature range, 25°C – 70°C at fixed concentration values of the complex as stated above, at fixed [SDS] = 2.00 x 10⁻⁴ mol dm⁻³. Activation energies were obtained from Arrhenius equation from the slope of a plot of In k_{obs} vs 1/T (K⁻¹) and the activation parameters were obtained from Erying's equation (Svirberly and Kundel, 1967).

III. RESULTS AND DISCUSSION

The observed rate constant of binding, k_{obs} was invariant with $Fe(Me_4phen)_3^{2+}$ at fixed SDS concentrations in neutral aqueous medium. This simply shows that the complex is located in the same region of the stern layer and that previous work by Ige and Soriyan, 1986 showed that the Iron(II) complex is stabilized with respect to dissociation in the micellar phase. The overall data of the rate of binding of the complex by SDS in neutral medium showed inhibition on

addition of the sodium dodecyl sulphate approaching saturation at higher [SDS] as shown in figure I. The reason is because as [SDS] increases the number of oligomers increases with the bulky complex experiencing steric hinderance not expected for monomeric SDS. Hence, this steric consideration predominates over hydrophobic character of the aggregates.

Moreover, rate of binding increased with increase in hydrogen ion concentration until k_{obs} attained a maximum at [H⁺] 2.00 x 10⁻⁴ mol dm⁻³ after which [H⁺] inhibites rate of binding as shown in figure II. Increase in rate of binding was attributed to the fact that as H⁺ was added, the –OSO3⁻ head group of the surfactant was readily protonated. The lauryl sulphonic acid is more hydrophobic than SDS, therefore rate of binding increases because of the enhanced hydrophobic interaction between the lauryl sulphonic acid and the Iron(II) complex however, k_{obs} increased until all the SDS was protonated. Beyond this saturation point, added protons remained in solution and increases the dielectric constant of the solution. This led to a decrease in the rate of binding and it is also significant to note that further increase in [H⁺] beyond saturation point led to repulsion between the incoming positively charged Iron(II) complex and the protons in the diffuse guoy-chapman layer, hence the rate of binding decreased.



Figure I: Plot of observed rate constant (k_{obs}) against [SDS] for the binding of Fe(Me₄phen)₃²⁺ with SDS, Temperature = 25°C.



Furthermore, hydroxyl inhibited the rate of binding as shown in figure III. Inhibition is due to increase in the dielectric constant of the medium as [OH] increases which consequently led to decrease in the hydrophobicity of the medium (Menger and Portony, 1969). Hence hydrophobic interaction between the metal complex and SDS was significantly reduced as [OH] increases. The rate of binding was catalysed in the presence of sodium benzoate (figure IV). The observed 83% increase in k_{obs} at the fixed lowest concentration of SDS and 14% increase at the highest fixed concentration of SDS within the same benzoate concentration range for the complex and general increase in the rate of binding is due to the orientation of the benzoate ion as suggested by previous kinetic data (Burrows et al., 1982) and confirmed by NMR data (Tachiyashiki and Yamatera, 1986). This unique orientation shows that phenyl group of the benzoate ion aligns below the head group of the SDS monomers due to its hydrophobic nature as shown in figure V. This orientation causes an increase in the negative charge on the pre-micelle resulting to increase in the rate of binding. Furthermore, rate of binding was inhibited in urea dependent study as shown in figure VI. The decrease in rate of binding in the presence of urea can be attributed to the fact that urea reduces the negative charge density on SDS by interaction through hydrogen bonding between its protons and SDS head group. Increase in urea concentration decreases the negative charge density on SDS which results to a decrease in the electrostatic attraction between the Iron(II) complex and the surfactant thereby leading to a



Figure IV: Plots of k_{obs} versus [C₆H₅COONa] for binding between Fe(Me₄phen)₃²⁺and SDS. \bigcirc [SDS] 2.00 x 10⁻⁴ mol dm⁻³ \blacktriangle [SDS] 3.00 x 10⁻⁴ mol dm⁻³, \bigcirc [SDS] 5.00 x 10⁻⁴ mol dm⁻³ and \blacksquare [SDS] 7.00 x 10⁻⁴











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decrease in rate of binding. However, partial neutralization of the negative charge density on SDS by the protons on urea should in turn increase the hydrophobicity of the medium. Obviously in this case decrease in electrostatic attraction predominates over increase in hydrophobicity.

Moreso, presence of urea would enhance steric hinderance and this added steric consideration has the additional effect of inhibiting the rate of binding with increase in urea concentration.

Furthermore, temperature dependent study as shown in Table I revealed the activation parameters.

Table 1. Activation parameters of omening of the complex with 5D5				
Substrate	Ea(kJmol ⁻¹)	ΔH^{\ddagger} (kJmol ⁻¹)	ΔS^{\ddagger} (kJK ⁻¹ mol ⁻¹)	ΔG^{\ddagger} (kJmol ⁻¹)
_	39.96	37.48	-9.69	58.23
Urea	30.28	27.80	-10.02	58.77
Benzoate ion	16.46	13.98	-10.13	57.29
OH	33.69	31.21	-9.91	58.94
H^+	26.82	24.34	-10.11	57.43

Table I. Activation parameters of binding of the complex with SDS

IV. CONCLUSION

It was shown that both electrostatic and hydrophobic interactions played significant role in the binding of metal chelate complexes with surfactants. The binding of the complex was inhibited by SDS concentration and independent of complex concentration. H^+ , OH^- , C_6H_5COONa and urea greatly affects the binding process either by electrostatic or hydrophobic interaction. The mechanism of binding is the same in all the systems due to the approximate invariance in the free energies of activation. The negative values of entropy of activation shows entropy decrease upon achieving the transition state, which often indicates an association mechanism.

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