

The Kinetics of Binding of Tris- (4, 7- Dimethyl-1, 10-Phenanthroline) Iron (II) Perchlorate with Sodium Dodecyl Sulphate

¹Latona D. F, ²Ige J, ³Soriyan O.O

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

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

Abstract: *The kinetics of binding of tris-(4, 7-dimethyl-1, 10-phenanthroline) iron (II) perchlorate with sodium dodecyl sulphate was investigated below the critical micelle concentration of the surfactant. The effects of additives like sodium benzoate, urea, H⁺ and OH⁻ on the binding due to hydrophobic/electrostatic interaction was studied. The reaction was monitored under pseudo-first order kinetics with a unicam UV-visible spectrophotometer. The binding of phenanthroline iron (II) complex was demonstrated by hydrophobic effect due to the presence of the phenanthroline ligands and by electrostatic interaction due to the +2 charge on the complex. The reaction was complex independent. General invariance in free energy of activation showed same mechanism for the reaction.*

Keywords: dimethyl 1-1, 10-phenanthroline, iron (II)

1. Introduction

Surfactants are chemicals which show the ability to adsorb at surfaces. They are therefore called surface – active agents. The surfaces (interfaces) at which they adsorb can either be between two liquids, between liquid and gas (air) or between solid and liquid (Warren and Buchanan, 2001). Despite that surfactants often are present in very small amounts in solution; they greatly affect the overall properties of the system because of their ability to adsorb at surfaces (Warren and Buchanan, 2001).

Surfactants are therefore sometimes referred to as “effect chemicals” and instead of using the general term surfactants, many surface – active compounds are named after the specific effect they show in solutions, such as dispersing agents, foaming agents, wetting agents, emulsifiers etc (Colgate and Bain, 2005). Surfactants that occur naturally, otherwise known as so-called – chemicals include simple lipids like carboxylic acid esters, complex lipids such as fatty acid esters containing phosphorus, nitrogen bases (Fendler and Fendler, 1975). While the synthetic surfactants are classified based on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion thereof; they may be classified as cationic, nonionic, amphoteric (zwitterionic) surfactants (Kurz, 1962; Attwood et al., 1970)

Generally, iron (II) complexes have d⁶ (t_{2g}⁴e_g²) and are high spin (Cotton and Wilkinson, 1972). They are generally kinetically labile because the complexes have little crystal – field stabilization. However, a few ligands such as 1, 10 – phenanthroline and its substituted derivatives interact sufficiently strong with metal centre to force spin pairing producing the kinetically inert t_{2g}⁶ configuration (Syke, 1970). Consequently, the aquation of resulting Fe(phen)₃²⁺ complexes and its derivatives are quite slow, but have been studied extensively in aqueous solutions and in aqueous organic solvent mixtures, though to a less extent in the latter.

2. Experimental

Tris-(4, 7 -dimethyl-1, 10-phenanthroline)iron(II) perchlorate was synthesized and purified as reported earlier (Shakhashuri and Gordon, 1964). The complex was characterized by its UV-visible spectra and the maximum absorption peak (λ_{max}) was determined to be 510 nm. Which was in agreement with the literature values (Shakhashuri and Gordon, 1964). Purified sodium dodecyl sulphate (99%) was used with further recrystallisation. The purity was confirmed by the determination of the critical micelle concentration in aqueous solution at 25°C. The value of 8.20×10^{-3} mol dm⁻³ obtained is in agreement with the literature value (Williams et al., 1985). Analytical grade (BDH), sodium hydroxide, sodium benzoate, sulphuric acid and urea were utilized.

3. Kinetics

Kinetic data were obtained by monitoring change in absorbance of ferric complex at absorption maximum (λ_{max}) as a function of time using unicam UV -visible spectrophotometer. The concentration of the complex was maintained at 1.80×10^{-5} mol dm⁻³. The concentration of sodium dodecyl sulphate ranged within (2.00×10^{-4} – 8.00×10^{-4} mol dm⁻³). The kinetic runs were performed under pseudo – first order kinetics and rate constants were obtained from the slope of $\ln(A_{\infty} - A_t)$ versus time. The effect of H⁺, OH⁻, C₆H₅COONa and urea on binding were investigated. The activation parameters were determined within the temperature range, 25°C – 70 °C at fixed concentration value of the complex (1.80×10^{-5} mol dm⁻³), at fixed [SDS]= 2.00×10^{-4} mol dm⁻³. Activation energies were obtained from Arrhenius equation from the slope of a plot of $\ln k^{obs}$ vs $1/T(K^{-1})$ and the activation parameters were calculated from Eyring's equation (Svirberly and Kundel, 1967).

4. Results and Discussion

The observed rate constant of binding, k_{obs} was in variant with the $Fe (Me_2phen)_3^{2+}$ at fixed SDS concentrations in neutral aqueous medium. Hence, there is an indication that the complex is located in the same region of the Stern layer. Rate of binding of the complex to SDS in neutral medium showed inhibition on addition of the sodium dodecyl sulphate approaching saturation at higher [SDS] as shown in figure I. This can be attributed to the fact that as [SDS] increases the number of oligomers increases with the bulky complex experiencing steric hindrance not expected for monomeric SDS. Therefore, this steric consideration predominates over the enhanced hydrophobic character of the aggregates. Moreover, rate of binding increased with increase in hydrogen ion concentration until k_{obs} attained a maximum at $[H^+] 1.00 \times 10^{-4} \text{ mol dm}^{-3}$ 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 $-SO_3^-$ head group of the surfactant was readily protonated. The lauryl sulphonic acid is more hydrophobic than SDS, therefore rate of binding increased because of the enhanced hydrophobic interaction between the lauryl sulphonic acid and the Iron(II) complex, however k_{obs} increased until all the SDS were protonated. Beyond this saturation point, an added proton remained in solution and increases the dielectric constant of the solution, which led to a decrease in the rate of binding. It is also significant to note that further increase in $[H^+]$ beyond the 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.

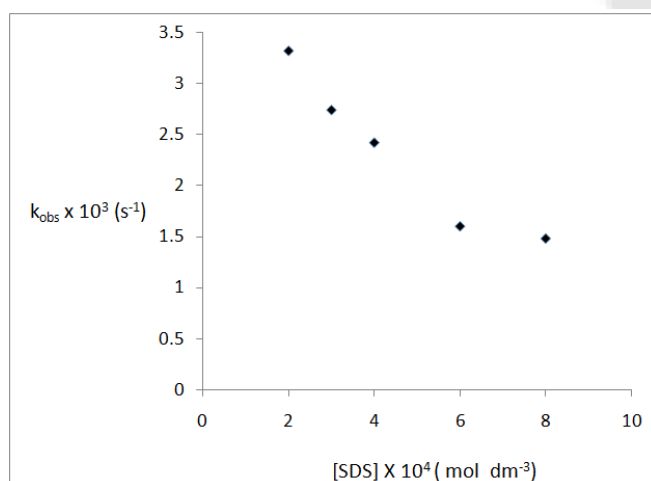


Figure 1: Plot of observed rate constant (k_{obs}) against [SDS] for the binding of $Fe (Me_2phen)_3^{2+}$ with SDS, Temperature = 25°C

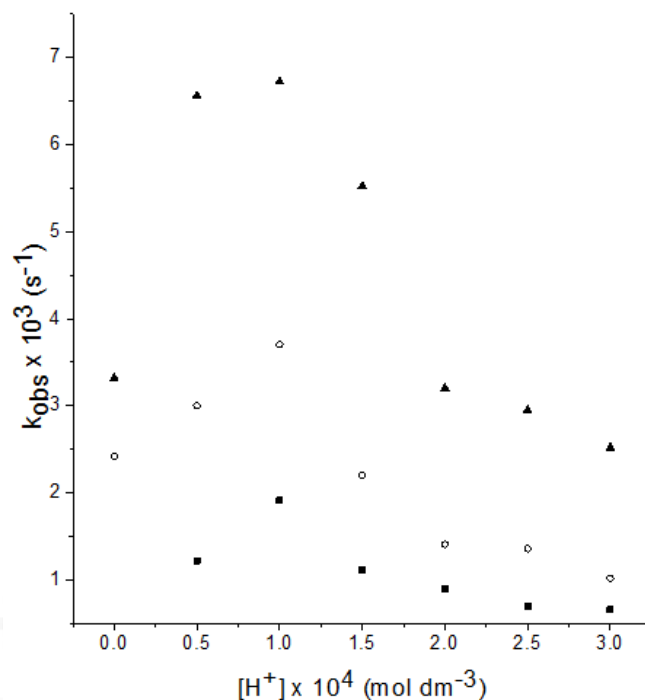


Figure 2: Plots of k_{obs} versus $[H^+]$ for binding between $Fe (Me_2phen)_3^{2+}$ and SDS

- ▲ [SDS] $2.00 \times 10^{-4} \text{ mol dm}^{-3}$
- [SDS] $4.00 \times 10^{-4} \text{ mol dm}^{-3}$
- [SDS] $6.00 \times 10^{-4} \text{ mol dm}^{-3}$

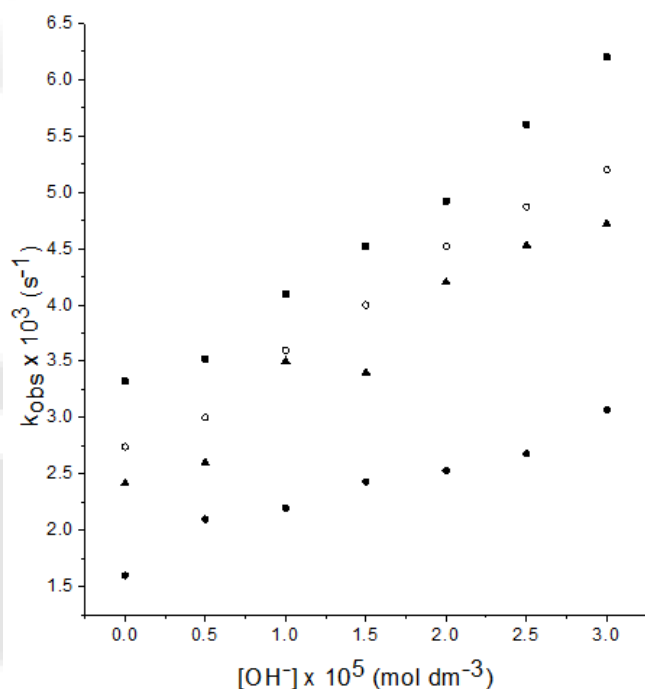


Figure 3: Plots of k_{obs} versus $[OH^-]$ for binding between $Fe (Me_2phen)_3^{2+}$ and SDS

- [SDS] $2.00 \times 10^{-4} \text{ mol dm}^{-3}$
- [SDS] $3.00 \times 10^{-4} \text{ mol dm}^{-3}$
- ▲ [SDS] $4.00 \times 10^{-4} \text{ mol dm}^{-3}$
- [SDS] $6.00 \times 10^{-4} \text{ mol dm}^{-3}$

Moreover, hydroxyl catalysed binding reaction as shown in figure III. Increase in rate of binding with $[OH^-]$ is attributed to a negatively charged complex anion (formed as a result of polymerization between perchlorate ion and hydroxyl ion) which allows for increased positive charge density on the metal centre of the complex. This thereby resulting to favourable electrostatic interaction between the Iron(II) metal centre and SDS. The rate of binding was catalysed in the presence of sodium benzoate (figure IV), which 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 align itself 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 density on the pre-micelle resulting to increase in coulombic or electrostatic attraction between the positively charged metal complex and the micellar surface, leading to increase in the rate of binding.

Furthermore, rate of binding was enhanced for urea dependent study as shown in figure VI. The reason is due to the removal of urea by ClO_4^- or vice-versa, leading to the formation of urea perchlorate (Rubstov et al., 1979). The removal of perchlorate ions will increase the positive charge density on the Iron (II) complex and this in turn would lead to increased electrostatic interaction between SDS and the metal ion.

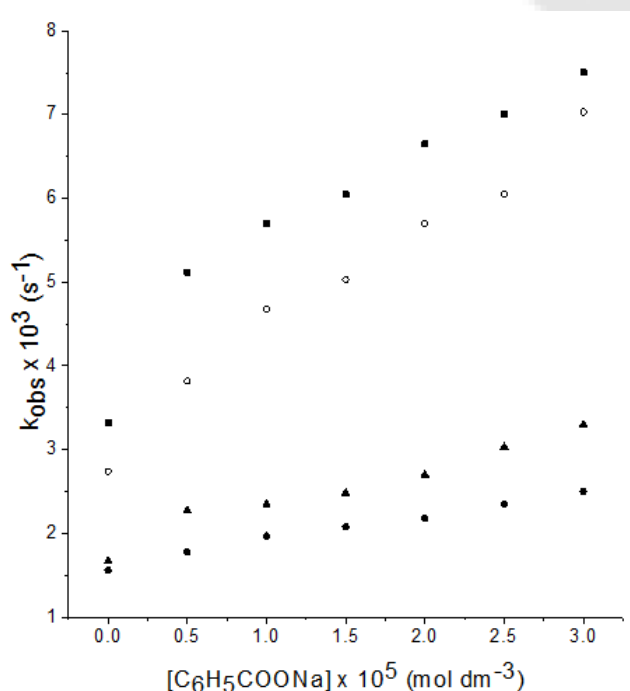


Figure 4: Plots of k_{obs} versus $[C_6H_5COONa]$ for binding between $Fe (Me_2phen)_3^{2+}$ and SDS.

- [SDS] 2.00×10^{-4} mol dm^{-3}
- [SDS] 3.00×10^{-4} mol dm^{-3}
- ▲ [SDS] 5.00×10^{-5} mol dm^{-3}
- [SDS] 7.00×10^{-4} mol dm^{-3} .

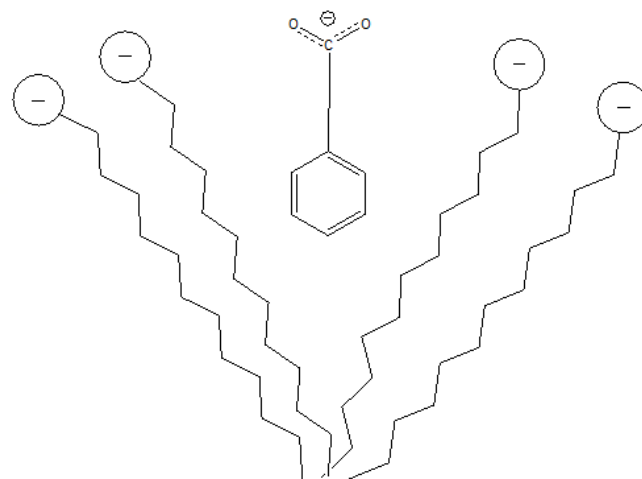


Figure 5: Benzoate ion – SDS molecule interaction

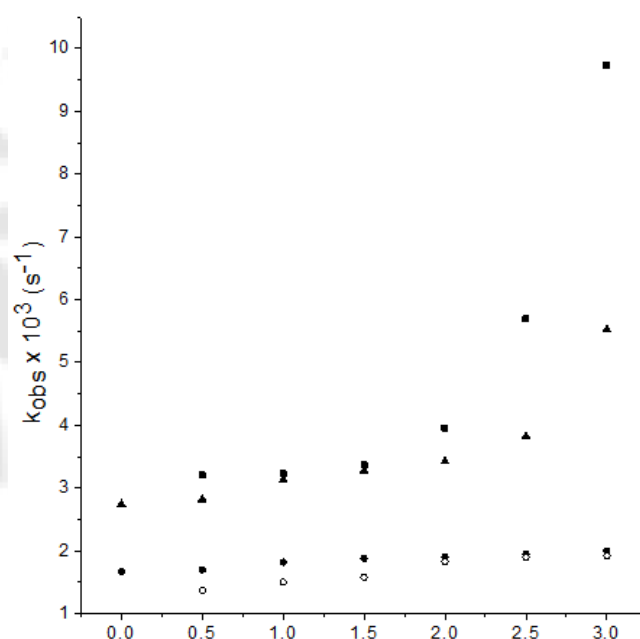


Figure 6: Plots of k_{obs} versus [urea] of binding between $Fe (Me_2phen)_3^{2+}$ and SDS.

- [SDS] 2.00×10^{-4} mol dm^{-3}
- ▲ [SDS] 3.00×10^{-4} mol dm^{-3}
- [SDS] 5.00×10^{-4} mol dm^{-3}
- [SDS] 7.00×10^{-4} mol dm^{-3}

The temperature dependent study as shown in Table I revealed the activation parameters. The observed slight invariance in the free energy of activation suggests same mechanism for the binding process.

Table 1: Activation parameters of binding of the complex with SDS

Substrate	Ea(kJmol ⁻¹)	ΔH^\ddagger (kJmol ⁻¹)	ΔS^\ddagger (kJK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJmol ⁻¹)
	23.88	21.40	-10.155	5.91
Urea	25.57	23.09	-10.0955	.48
Benzoate ion	16.26	13.78	-10.355	4.19
OH ⁻	20.92	18.44	-10.2154	.94
H ⁺	18.86	16.38	-10.32	56.00

5. Conclusion

It was evident that both the electrostatic and hydrophobic interaction between the Iron (II) complex and sodium dodecyl sulphate played major role in the binding process. The binding was enhanced in the presence of sodium benzoate, OH⁻ and urea. However, in H⁺, the binding reaction was enhanced at low [H⁺] and inhibited at [H⁺] > 1.00 x 10⁻⁴ mol dm⁻³.

The binding study was independent of complex concentration. The negative values of entropy of activation show entropy decrease upon achieving the transition state, which often indicates an association mechanism. Invariant free energies of activation suggest common mechanism.

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