

The Effect of Substrates on the Binding of Tris- (4,7- Dimethyl -1,10 Phenanthroline) Iron(II) Perchlorate with Surfactants.

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Abstract

Binding studies were carried out as a function of the concentration of NH_4Cl , $(\text{C}_2\text{H}_5)_4\text{NI}$ and $(\text{C}_4\text{H}_9)_4\text{NI}$ at room temperature and change in absorbance were taken at 520nm with a UV – visible spectrophotometer. It was found that the higher the concentration of the substrate the greater the binding constants. Consequently, the higher the hydrophobicity of the substrate the lower the binding constant in the case of hexadecyl trimethyl ammonium bromide, CTAB and the reverse for sodium dodecyl sulphate, SDS surfactant. The binding constants were determined by employing double reciprocal plot. Binding is attributed to hydrophobic/electrostatic interaction between the Iron(II) complex and the surfactants.

Keywords: CTAB; SDS; Tris-(4,7-dimethyl-1,10-phenanthroline) Iron(II) Perchlorate

Introduction

Ching-Fawu et al (1995) worked on the determination of the binding constant of imidazole and Histidine with immobilized Cu(II) by differential UV spectroscopy. It was reported that there was no obvious effect of temperature on the binding constant because of the complexity of binding mechanism.

Kokugan et al (1995) investigated the measurement of binding constant of cyclodextrin by ultrafiltration, which is a new method of measuring binding constants. Elbs and Brock (2003) determined the binding constants on micro arrays with confocal fluorescence detection. It was employed for the determination of binding of receptor-ligand interaction in a micro array format.

Tedesco et al (2003) determined the binding constant of biocompatible ferrite-based magnetic fluids to serum. The interaction between molecular coated magnetic nanoparticles and serum albumin protein (BSA) through the fluorescence quenching of the tryptophan residue present in BSA after the binding of Me-MNPS to specific sites was investigated.

Furthermore, Sowell et al (1990) worked on the binding constant determination of drugs towards subdomain(III) of human serum albumin by near-infrared dye-displacement capillary electrophoresis. It was reported that the dye-displacement technique uses a competitive-type interaction between the drug of interest and a dye probe to arrive at a binding constant. It was stated that the dye displacement technique has advantage over current electrophoresis based technique in that it was faster and uses less reagent.

The effects of putrescence, spermidine and spermine on membrane-bound acetylcholinesterase human erythrocyte and the solubilized enzyme of the electric organ of the electric eel were investigated by Kossorotow et al., 1974. However, this report investigated the binding constants of Tris-(4,7 dimethyl-

1,10 – phenanthroline) Iron(II) Perchlorate with a cationic surfactant, hexadecyl trimethyl ammonium bromide(CTAB) and an anionic surfactant, sodium dodecyl sulphate(SDS) with/without the presence of some substrates like NH_4Cl , $(\text{C}_2\text{H}_5)_4\text{NI}$, and $(\text{C}_4\text{H}_9)_4\text{NI}$ using double reciprocal plot analysis.

Experimental

Binding of Iron(II) complex with the surfactants were done using a unicam UV- visible spectrophotometer at 25°C . The analyses were carried out by using double reciprocal plot. The absorbance were taken at the maximum absorption peak of the Iron(II) complex (λ_{max}), 520nm. Binding was done at fixed concentration of the Iron(II) complex of $1.49 \times 10^{-5} \text{ mol dm}^{-3}$ and the concentrations of the surfactants taken were below their critical micelle concentrations (CMC) $9.15 \times 10^{-5} \leq [\text{CTAB}] \leq 5.49 \times 10^{-4} \text{ mol dm}^{-3}$; $2.60 \times 10^{-4} \leq [\text{SDS}] \leq 2.08 \times 10^{-3} \text{ mol dm}^{-3}$. Increase in absorbance as a result of binding until a plateau was observed.

Determination of Binding constant

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

α = Fraction bound of complex onto the surfactant.

A_0 = Absorbance when no surfactant was added.

A_∞ = Absorbance when Iron(II) complex solution was saturated with surfactant.

A = Absorbance when known amount of surfactant were added.

The total Iron(II) complex was obtained using molar-extinction coefficient at λ_{max} . The concentration of free Iron(II) complex $[\text{Fe}^{2+}]_f$ was obtained from:

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

$$[\text{Fe}^{2+}]_{\text{bound}} = \alpha[\text{Fe}^{2+}]_T$$

$$v = \frac{[\text{Fe}^{2+}]_{\text{bound}}}{[\text{surfactant}]_{\text{Total}}}$$

v = The average number of molecules of Iron(II) complex combined with each surfactant.

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

$$\text{slope} = \frac{1}{n_s K}$$

$$\text{Intercept} = \frac{1}{n_s}$$

$$n_s = \frac{1}{\text{Intercept}}$$

$$\frac{1}{v} \text{ against } \frac{1}{[\text{Fe}^{2+}]_f}$$

Where, K = Binding constant and n_s = sites per monomer

Results and Discussion

Double reciprocal plot of $1/v$ against $1/[Fe^{2+}]_f$ gave a straight line graph with slope $1/n_s K$. In the absence of substrates, binding was faster in SDS (1.32×10^5) than CTAB (1.01×10^5) showing that electrostatic attraction takes precedence over hydrophobic interaction between the Iron(II) complex and the surfactants in the absence of substrates. There was a general increase in binding with increase in the concentration of the substrates. Binding was in the order: $NH_4Cl > (C_2H_5)_4NI > (C_4H_9)_4NI$ in CTAB and $(C_4H_9)_4NI > (C_2H_5)_4NI > NH_4Cl$ in SDS. Binding in the presence of NH_4Cl was greater in CTAB than SDS (Table I). Conversely, binding was reported to be faster in SDS than CTAB in the presence of $(C_2H_5)_4NI$ as shown on Table II. Furthermore, binding constants were reported to be conspicuously higher in SDS than CTAB in the presence of $(C_4H_9)_4NI$ (Table III). Binding of Iron(II) complex with CTAB could best be explained in terms of hydrophobic interaction, while in SDS it is believed that the electrostatic interaction takes precedence over hydrophobic interaction. The binding trend between Fe(II) complex and SDS in the presence of the substrates could be due to high repulsion between the substrate molecules and Fe(II) complex. The higher the substrate molecular size the greater the repulsive effect between the substrate molecules and Fe(II) complex, thereby causing an effective attraction between Fe(II) complex and the negatively charged SDS molecules. Conversely, the binding order between Fe(II) complex and CTAB in the presence of the substrates is primarily due to steric hindrance which reduces the hydrophobic interaction between the Fe(II) and CTAB. The higher the molecular size of the substrates, $(C_4H_9)_4NI > (C_2H_5)_4NI > NH_4Cl$ the greater the steric hindrance for hydrophobic interaction between Fe(II) complex and CTAB.

Table 1 The effect of NH_4Cl on the Binding of Tris-(4,7 dimethyl- 1,10 – phenanthroline Iron(II)perchlorate with CTAB and SDS.

$[NH_4Cl] \times 10^2$ (Mol dm ⁻³)	K/10 ⁶	
	CTAB	SDS
3.0	1.65	0.125
2.0	0.957	0.100
1.0	0.884	0.0796
0.5	0.526	0.0746
0.1	0.136	0.0444

Table 2 The effect of $(C_2H_5)_4NI$ on the Binding of Tris- (4,7 dimethyl 1,10- phenanthroline) Iron(II)perchlorate with CTAB and SDS.

$[C_2H_5)_4NI] \times 10^2$ (M)	K/10 ⁵	
	CTAB	SDS
3.0	1.42	1.41
2.0	0.877	1.09
1.0	0.495	0.821
0.5	0.319	0.758
0.1	0.234	0.478

Table 3 The effect of $(C_4H_9)_4NI$ on the Binding of Tris- (4,7 dimethyl - 1,10-phenanthroline)Iron(II) perchlorate with CTAB and SDS.

$[(C_4H_9)_4NI] \times 10^2$	$K/10^5$	
	CTAB	SDS
3.0	0.116	2.15
2.0	0.111	1.67
1.0	0.0679	1.15
0.5	0.0654	1.02
0.1	0.0548	0.444

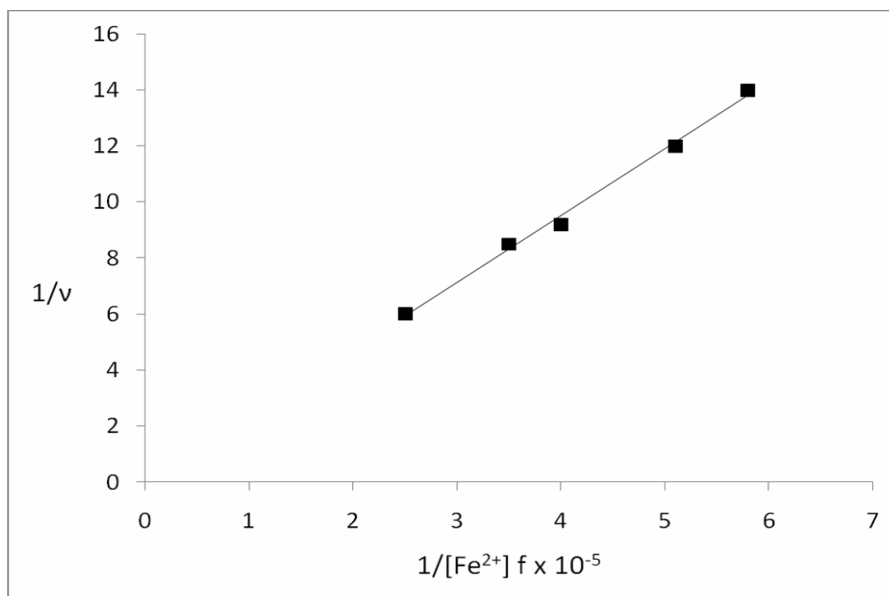


Fig. I: Plot of $1/v$ against $1/[Fe^{2+}]f$ for the binding of CTAB with Tris (4,7 dimethyl- 1,10 phenanthroline)Iron(II) perchlorate in 0.001M $(C_4H_9)_4NI$

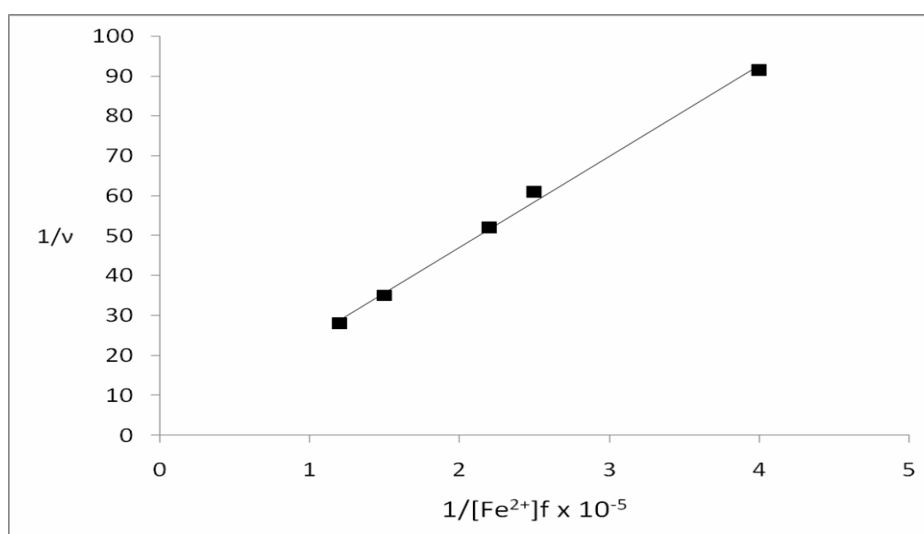


Fig.II: Plot of $1/v$ against $1/[Fe^{2+}]f$ for the binding of SDS with Tris(4,7 dimethyl- 1,10 - phenanthroline)Iron(II) perchlorate in 0.001M $(C_2H_5)_4NI$

Conclusion

Interaction between metal ion complex and surfactants has been shown to be either by hydrophobic or electrostatic interaction. In the case of the interaction between the metal ion complex with a positively charged surfactant like CTAB, it is believed that the hydrophobic interaction would take precedence over electrostatic attraction. Conversely, the interaction of the metal complex ion with an anionic surfactant like SDS, it is hoped that electrostatic attraction would dominate over hydrophobic interaction.

Reference

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