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Investigation of the binding of some Iron(II) complexes of phenanthroline and bipyridyl ligands with cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate(SDS) surfactants

Oladega O. Soriyan*, Sanusi, O. Owoyomi and Jide Ige

Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

Abstract

The interactions between the various Iron (II) polypyridyl complexes and Cetyltrimethyl ammonium bromide (CTAB), a cationic and Sodium dodecyl sulphate (SDS) an anionic were investigated using UV absorption spectroscopy. The binding constant was determined using Scatchard method. In CTAB, the binding is essentially hydrophobic but the electrostatic interaction contribution to the binding from the positively charged quaternary ammonium head group and π-electron rich phenanthroline ligands is also significant. The binding constant in SDS is consistently higher, a direct reflection of stronger electrostatic interaction than in CTAB.

Key words: Phenathroline, bipyridyine Iron(II) complex ion, surfactants, CTAB and Sodiun dodecylsulphate (SDS).

INTRODUCTION

A lot of work had been reported on the micellar catalysis of dissociation and racemization of systems containing coordination compounds of aromatic nitrogen-donor ligands such as 1,10-phenanthroline and 2,2$'$-bipyridine in various surfactant solutions [1-7]. Each of the surfactant studied affects the rate majorly at concentration below the critical micelle concentration (cmc). The rate change is explained by favourable binding between the surfactant aggregates and Iron (II) complex and the distribution of the iron complex between the micellar phase and the bulk water phase [3-7]. There have been various kinetic model used to explain the various data obtained and from this the binding constants have been determined [4-6] . The report on the binding using a non-kinetic method is rather scanty. This present study is aim at investigating the effect of binding of various substituent phenathroline and bipyridyine Iron (II) complex ion with surfactants hexadecyltrimethylammonium bromide (CTAB) and Sodiun dodecylsulphate (SDS) by spectrophotometric method. A comparison of the effect of substituent on the binding constant will show the role of the charge and the hydrophobic group in the interaction.

MATERIALS AND METHODS

Materials

The perchlorate of Iron(II) phenanthroline complexes {ie.$[Fe(phen)_3](ClO_4)_2$, $[Fe(4,7\text{-}Me_2phen)_3](ClO_4)_2$, $[Fe(5,6\text{-}Me_2phen)_3](ClO_4)_2$ and $[Fe(Me_4phen)_3](ClO_4)_2$} were obtained from G. F. Smith chemical company and were used without further recrystallisation. The dicyanobis-(phenanthrolineIron(II)complexes{$[Fe(phen)_2(CN)_2]$ and $[Fe(4,7\text{-}Me_2phen)_2(CN)_2]$} and the bipyridyl Iron(II)complexes {$[Fe(bipy)_3]^{2+}$ and $[Fe(4,4'\text{-}Me_2bipy)_3]^{2+}$} were prepared from the analar grade of the phenathroline ligand according to the literature [8,9]. All the complexes were characterized by their UV spectra. Their UV-Visible spectrum gave molar extinction coefficients (at various λ_{max} of each complex) which were in excellent agreement with the literature value [8-9].

The hexadecyltrimethylammonium bromide (CTAB) were obtained with the highest available purity from Fluka and used as received. The purity of the surfactant (CTAB) was verified by determining its critical micelle concentration. Specially purified Sodium dodecyl sulphate(B.D.H) (99% purity) was used without further recrystallization. The purity was ascertained by determination of the critical micelle concentration in aqueous solution at 25^0C which correlated with the literature value [10]. The water used throughout was glass distilled. Iron(ll) complexes concentrations were fixed at 1.45×10^{-5} M except where stated otherwise.

The stock solutions were kept in the refrigerator to further reduce any aquation. These solutions were usually used up within two to three days of preparation to minimize possible errors from slight spontaneous aquation of the complexes which had been observed in previous work [4-7]. Surfactant solutions were usually prepared fresh to avoid ageing of the micelle solution.

Methods

The binding interactions were followed by measuring the absorbance of iron(ll) complexes at their various λ_{max} as a function of surfactant concentration using Unicam α-Heλios Spectrophotometer, V2.05. And the analyses were done using Scatchard method [11]. The results obtained were checked with another method, the Hills method [12]; the results from the two methods were in concordance.

The fraction of Iron(ll) complex ions bound (α) to the surfactant molecules was calculated from:

$$\alpha = \frac{A - A_o}{A_\infty - A_o} \qquad 1$$

where, A_o= absorbance at λ_{max} of the complex when no surfactant was added

A_∞= absorbance at λ_{max} of the complex when Iron(II) complex was saturated with surfactant

A= absorbance at λ_{max} of the complex when known amounts of surfactant were added Concentration of total Iron(ll) complex, $[Fe^{2+}]_T = 1.45 \times 10^{-5}$ M

The concentration of free Fe(II), $[Fe^{2+}]_f$ was obtained from:

$$\left[Fe^{2+}\right]_f = \left[Fe^{2+}\right]_T - \alpha\left[Fe^{2+}\right]_T \qquad 2$$

The average number of molecules of iron(ll) complex that combined with each CTAB molecule (ν) was obtained by

$$\nu = \frac{\left[Fe^{2+}\right]_{bound}}{[Surfac\tan t]_{total}} = \frac{\alpha\left[Fe^{2+}\right]_T}{[Surfac\tan t]_{total}} \qquad 3$$

The plot of $1/\nu$ versus $1/\left[Fe^{2+}\right]_f$ was made, the binding constant K and the number of binding sites per surfactant monomer, N_s were calculated from the slope and the intercept using the Scatchard equation

$$\frac{1}{\nu} = \frac{1}{N_s} + \frac{1}{N_s K\left[Fe^{2+}\right]_f} \qquad 4$$

A typical plot of $1/\nu$ against $1/[Fe(II)\ complex]_{free}$ gave a straight line (Figure1). The results of the binding constants (K) and the number of binding sites per surfactant monomer (N_s) in CTAB and SDS were summarized in Tables 1 and 2.

Determination of c.m.c of CTAB and SDS in the presence of Iron(ll) complexes
The determination of c.m.c was based on the principle that the change in physical property of a detergent or surfactant solution undergoes a sharp break at or around the c.m.c as its

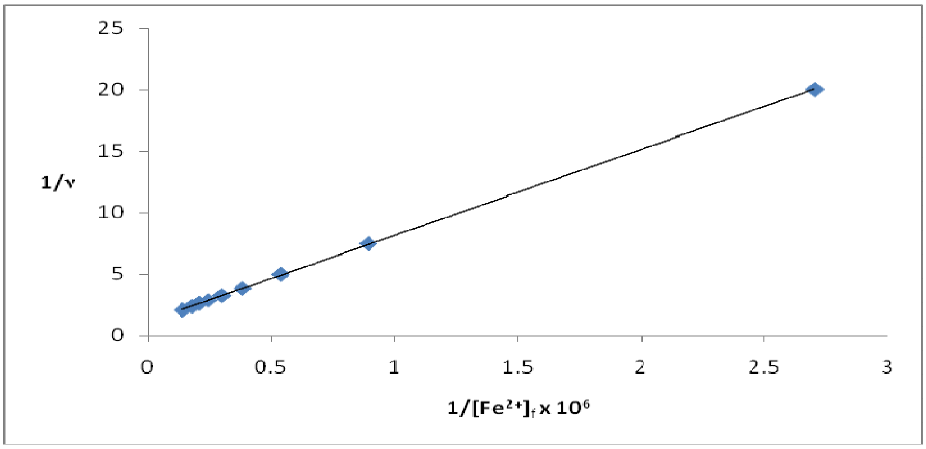

Figure 1: A typical plot of $1/\nu$ against $1/[Fe(II)\ complex]_{free}$ at 25°C

concentration increases [13]. The physical property employed in this determination is electrical conductivity (µScm^{-1}). This was done by varying the concentration of surfactant in the presence of a constant concentration of each Iron(II) complex using Model 4330 conductivity/pH meter at 25^{0}C. The cell constant was 1.00 m. The result CTAB and SDS were summarized in Tables 1 and 2. The binding constants in un-substituted phenatholine and bipyridyl Iron (II) complexes could not be determined by this method as there was no appreciable change in absorbance.

Table 1:The result of binding constants and number of binding site per monomer in the interaction of CTAB and phenathroline complexes at 25^{o}C

	Metal Complexes	**Binding constant (K)**	**c.m.c(mol dm^{-3})**	**No of binding site per surfactant monomer (N_s)**
1.	$[Fe(Me_4phen)_3]^{2+}$	6.35×10^5	2.0×10^{-4}	7.87
2.	$[Fe(phen)_3]^{2+}$	$^*1.70 \times 10^4$	8.8×10^{-4}	-
3.	$[Fe(5,6\text{-}Me_2phen)_3]^{2+}$	3.42×10^5	4.5×10^{-4}	0.49
4.	$[Fe(4,7\text{-}Me_2phen)_3]^{2+}$	1.66×10^5	4.9×10^{-4}	0.86
5.	$[Fe(4,7\text{-}Me_2phen)_2(CN)_2]$	4.80×10^5	3.5×10^{-4}	6.94
6.	$[Fe(phen)_2(CN)_2]$	2.08×10^5	4.7×10^{-4}	5.34
7.	$[Fe(4,4'\text{-}Me_2bipy)_3]^{2+}$	5.00×10^4	7.0×10^{-4}	10.00
8.	$[Fe(bipy)_3]^{2+}$	-	8.9×10^{-4}	-

[*] *The binding was from the kinetic data from our previous work [4] as there was no appreciable change in absorbance using this method.*

Table 2:The result of binding constants and number of binding site per monomer in the interaction of SDS and phenathroline complexes at 25^{o}C

	Metal Complexes	**Binding constant (K)**	**c.m.c(mol dm^{-3})**	**No of binding site per surfactant monomer (N_s)**
1.	$[Fe(Me_4phen)_3]^{2+}$	9.44×10^5	5.90×10^{-4}	10.60
2.	$[Fe(phen)_3]^{2+}$	-	8.10×10^{-4}	-
3.	$[Fe(5,6\text{-}Me_2phen)_3]^{2+}$	9.72×10^5	6.10×10^{-3}	10.29
4.	$[Fe(4,7\text{-}Me_2phen)_3]^{2+}$	8.91×10^5	6.30×10^{-3}	11.2
5.	$[Fe(4,7\text{-}Me_2phen)_2(CN)_2]$	4.99×10^5	6.50×10^{-3}	10.12
6.	$[Fe(phen)_2(CN)_2]$	4.38×10^5	6.75×10^{-3}	11.40
7.	$[Fe(4,4'\text{-}Me_2bipy)_3]^{2+}$	4.05×10^4	6.80×10^{-3}	12.25
8.	$[Fe(bipy)_3]^{2+}$	-	8.9×10^{-4}	-

DISSCUSSION

The binding of the Fe(II) complexes with CTAB is essentially hydrophobic but strong interaction of quaternary ammonium head group with π-electron system of aromatic groups of the ligands in the Iron(II) complex have been reported in literature for some systems [13].

Ordinarily repulsion between the quarternary ammonium head group of CTAB and the positively charged Fe(II) complex is expected. However binding is strongly due to hydrophobic interaction between the hydrophobic tail of CTAB and bulky phenanthroline ligands of Fe(II). This is predominant but the electrostatic interaction contribution to the binding from the positively charged quanternary ammonium head group and π-electron rich phenanthroline ligands cannot be ignored.

For the Fe(II) phenanthroline complexes the binding constant is in the order:

$$\left[Fe(phen)_3\right]^{2+} < \left[Fe(4,7-Me_2phen)_3\right]^{2+} < \left[Fe(5,6-Me_2phen)_3\right]^{2+} < \left[Fe(3,4,7,8-Me_4phen)_3\right]^{2+}$$

$Fe(phen)_3^{2+}$ is the least hydrophobic with no methyl substituents. The higher electron density on the central aromatic ring due to the presence of methyl groups in the 5 and 6 positions makes the $[Fe(5,6\text{-}Me_2phen)_3]^{2+}$ to be more hydrophobic than the $[Fe(4,7\text{-}Me_2phen)_3]^{2+}$.

The variation in c.m.c. is in the order :

$$\left[Fe(3,4,7,8-Me_4phen)_3\right]^{2+} < \left[Fe(5,6-Me_2phen)_3\right]^{2+} < \left[Fe(4,7-Me_2phen)_3\right]^{2+} < \left[Fe(phen)_3\right]^{2+}$$

in conformity with available literature data for c.m.c. hydrophobicity trend [1,14-15].

For the cyano –phenanthroline mixed ligand complexes, binding constant is in the order :

$$\left[Fe(phen)_3\right]^{2+} < \left[Fe(phen)_2(CN)_2\right] < \left[Fe(4,7-Me_2phen)_2(CN)_2\right]$$

in excellent agreement with the trend in hydrophobic character. The positive charge on $Fe(phen)_3^{2+}$ makes it less hydrophobic than the cyano neutral complexes. The c.m.c. with increasing hydrophobicity [2,14-15] i.e

$$\left[Fe(4,7-Me_2phen)_2(CN)_2\right] < \left[Fe(phen)_2(CN)_2\right] < \left[Fe(phen)_3\right]^{2+}$$

The number of binding sites per monomer obtained from the Scatchard plots show a high variation in the position of the di-methyl substituents, that is

$\left[Fe\left(3,4,7,8-Me_4phen\right)_3\right]^{2+} < \left[Fe\left(5,6-Me_2phen\right)_3\right]^{2+} > \left[Fe\left(4,7-Me_2phen\right)_3\right]^{2+}$

The same trends are found in SDS micelle, an anionic surfactant for which the binding is a factor significant of both hydrophobic and electrostatic. The electrostatic interaction has significantly increased the binding as reflected in higher values of $K_{binding}$.

Table 3 shows the increased binding ratio K_{br} defined by

$$K_{br} = \frac{K_{binding}(in\ SDS)}{K_{binding}(in\ CTAB)}$$

The binding constant in SDS is consistently higher, a direct reflection of stronger electrostatic interaction than in CTAB. The increased binding factor is however least for the most hydrophobic complex and highest for the least hydrophobic. This shows that the electrostatic contribution to binding decreases with increasing hydrophobic character of the complex. For the neutral mixed cyano-phenathroline complexes this same trend is maintained.

The cmc lowering is more pronounced in CTAB than in SDS. Since hydrophobic interaction is more pronounced in CTAB, it is deduced from this work that hydrophobic interaction lowers cmc more than electrostatic interaction.

Table 3: The Binding factor K_{br} and cmc lowering as a function of the various complexes

	Metal Complexes	**Binding Factor K_{br}**	$* \frac{c.m.c(in\ water)}{c.m.c(in\ substrate)}$	
			SDS	CTAB
1	**[**$Fe(Me_4phen)_3]^{2+}$	1.5	0.73	0.22
2	**[**$Fe(phen)_3]^{2+}$	-	1.00	0.97
3	**[**$Fe(5,6\text{-}Me_2phen)_3]^{2+}$	2.8	0.75	0.49
4	$[Fe(4,7\text{-}Me_2phen)_3]^{2+}$	5.4	0.78	0.54
5	$[Fe(4,7\text{-}Me_2phen)_2(CN)_2]$	1.0	0.80	0.36
6	$[Fe(phen)_2(CN)_2]$	2.1	0.83	0.52
7	$[Fe(4,4'\text{-}Me_2bipy)_3]^{2+}$	-	0.84	0.77
8	$[Fe(bipy)_3]^{2+}$	-	1.00	0.98

**c.m.c of SDS in water = 8.1 x 10*$^{-3}$*M [4]*
c.m.c of CTAB in water = 9.1 x 10^{-4}*M [ ]*

In Table 3, the observation that no increase is observed in $\left(\frac{cmc(in\ water)}{cmc(in\ surfac\tan t)}\right)$ any of the surfactants confirms the predominance of hydrophobic interaction over electrostatic interaction in the evolution of the micelle.

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