



Dissociation Constant of Sodium Dodecyl Sulphate with Tris-(1,10-Phenanthroline)Iron(II) Complexes and Activation Parameters of Binding

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$\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$,

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phenanthroline)Iron(II) Perchlorate,

$\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$,

Sodium Dodecyl Sulphate, SDS,

Critical Micelle Concentration, CMC.

ABSTRACT

The temperature dependent study was investigated by using a UV-Visible spectrophotometer. Activation parameters such as energy of activation E_a , free energy of activation ΔG^\ddagger , entropy of activation ΔS^\ddagger and enthalpy of activation ΔH^\ddagger were obtained from Eyring's equation. The effect of substrates on the activation energy were in the order: benzoate ion > H^+ > urea > OH^- for Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)Iron(II) Sulphate, $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$ and benzoate ion > H^+ > OH^- > urea for Tris-(4,7-dimethyl-1,10-phenanthroline)Iron(II) Perchlorate, $\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$. Higher values of ΔH^\ddagger was observed in $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$ in all substrates. The rate constants of dissociation were obtained from earlier published results of rate constants of binding and binding constants. Dissociation constants generally decreased with increase in the concentration of the surfactant, SDS. Higher rate constant of dissociation was observed in SDS- $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$ than SDS- $\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$ in all the substrates.

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Introduction

Surfactants are chemicals which adsorb at surfaces. They have been extensively employed in a lot of kinetic studies. Surfactants have been established to inhibit the alkaline KMnO_4 oxidation of disaccharides (Tripathi and Upadhyah, 2013). Hetero Diels-Alder reaction have been studied in surfactant solutions (Lu et al., 2013). Surfactant effect on kinetic reaction of some sulphanamides with p-Dimethylamino benzaldehyde have been investigated (Khalil and Al-khoro, 2006). Trace metal ions have been determined kinetically by using surfactants (Stoyanova and Alexiev, 2005). Kinetic study of malachite green fading have been studied in the presence of neutral and charged surfactants (Samiey and Toosi, 2009). It is of interest that the oxidation of aldehydes in the presence of surfactant have been reported (Ahmad and Siddiqui, 2004).

Furthermore, it has been found that non-ionic surfactant triton x-100 acts as an efficient catalyst for the oxidation of D-maltose (Singh, 2014). Surfactants have been investigated to play an inhibitory role in the denitrification process taking place with the involvement of *Bacillus licheniformis* bacteria (Seifert and Domka, 2005). Spectrophotometric determination of Dissociation constant of fluorescein in micellar media has been investigated (Niazi et al., 2009). The study of the racemization and dissociation of Tris(1,10-phenanthroline)-iron(II) in the presence of alkali metal bromides, symmetrical tetraalkylammonium bromides and alkyltrimethylammonium bromide revealed that the alkali-metal bromides did not affect the racemization rate, but they decrease the dissociation rate and that the retarding effect increased with increasing bromide concentrations and decreased in the order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ (Tachiyashiki and Yamatera, 1982). The dissociation constants of 2- and 4- hydroxybenzoic acids and methyl, ethyl,

propyl and butyl esters of 4-hydroxybenzoic acid were determined in aqueous and micellar solution of sodium dodecyl sulphate (SDS) and Brij 35. It was reported that micelle concentration of surfactant influences the apparent dissociation constant to a greater extent than the monomeric form of surfactants (Vlasenko et al., 2009).

Surfactants used in this study included, Sodium dodecyl (lauryl)sulphate, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}^+$ which is an anionic surfactant and hexadecyl trimethyl ammonium bromide(CTAB) which of course is a cationic surfactant, $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$. In order to conclude the binding study of sodium dodecyl sulphate with Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)Iron(II) Sulphate and Tris-(4 dimethyl-1,10-phenanthroline)Iron(II) Perchlorate. It is noteworthy to determine the dissociation constants from earlier reports on the kinetics of binding and the determination of binding constants of these reactions (Latona et.al., 2013 : Latona et.al., 2014).

Materials

Synthesis of Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) sulphate

Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) sulphate was synthesized by dissolving a mixture of 0.3985 g ($\approx 1.686 \times 10^{-3}$ mole) of 3, 4, 7, 8 tetramethyl (1, 10-phenanthroline) ligand and 0.2204 g ($\approx 5.621 \times 10^{-4}$ mole) of ferrous ammonium sulphate ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in 5 ml of distilled water in a beaker. The resulting dark red solution was heated. Then the solution was stirred briefly and allowed to cool at room temperature. It was later left to dry in a dessicator.

Synthesis of Tris-(4,7- dimethyl-1,10-phenanthroline)iron(II)perchlorate

Tris - (4,7 dimethyl - 1,10 - phenanthroline)iron(II) perchlorate was synthesized by dissolving 0.354 g (1.686×10^{-3} mole)

of 4,7 dimethyl – 1,10 –phenanthroline) ligand and 0.204 g (5.621×10^{-4} mole) of ferrous perchlorate ($\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$) in 5 ml of distilled water in a beaker. The resulting dark red solution was heated to just below boiling point. The solution was stirred briefly and allowed to cool at room temperature. It was later left to dry in the dessicator.

Preparation of stock solution of 1,10-phenanthroline iron (II) complexes.

A stock solution of (1,10-phenanthroline)iron(II) complexes was prepared by dissolving 0.010 g of the complex in 25 ml standard flasks and making up the solution to the mark with distilled water. The concentrations were determined by diluting the stock solution and taking the absorbances at the maximum absorption peak (λ_{max}).

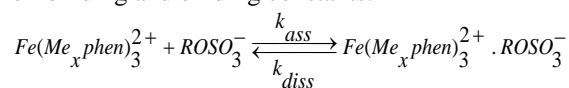
The concentrations of the stock solutions were checked each day to determine if any significant aquation had taken place. These were corrected before each run. The stock solutions were kept in the refrigerator to retard any further aquation, although the stock solution kept in the refrigerator was used usually within two or three days of preparation in order to minimize possible errors from slight spontaneous aquation of the complex. Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)Iron(II) Sulphate, $[\text{Fe}(\text{Me}_4\text{phen})_3]\text{SO}_4$ and Tris-(4,7-dimethyl-1,10-phenanthroline)Iron(II) Perchlorate, $[\text{Fe}(\text{Me}_2\text{phen})_3](\text{ClO}_4)_2$ were synthesized and purified according to the literature (Shakhashuri and Gordon, 1964). The complexes were characterized by their UV-visible spectra. The maximum absorption peaks (λ_{max}) determined were 500nm and 510nm 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. These were in excellent agreement with the literature values (Shakhashuri and Gordon, 1964). Purified sodium dodecyl sulphate (99%) was used without further recrystallization. The purity was ascertained by determination of the critical micelle concentration in aqueous solution at 25°C. The value of $8.20 \times 10^{-3} \text{ mol dm}^{-3}$ obtained is in consonance with the literature value (Williams et al., 1985).

Analar grade (BDH) sodium hydroxide (NaOH), sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$), tetraoxosulphate(VI) acid (H_2SO_4) and urea ($(\text{NH}_2)_2\text{CO}$) were utilized.

Experimental

Determination of rate constants of dissociation

Determination of rate constants of dissociation were obtained from earlier published kinetic results on rate constants of binding and binding constants.



$$x = 2 \text{ or } 4$$

$$K = \frac{k_{\text{ass}}}{k_{\text{diss}}} \quad ; \quad k_{\text{diss}} = \frac{k_{\text{ass}}}{K}$$

Where,

K = binding constant

k_{ass} = observed rate constant of binding (s^{-1})

k_{diss} = rate constant of dissociation (s^{-1})

Determination of activation parameters

The rate constants of binding were determined within the temperature range, 25°C- 70°C at fixed concentration values of the Iron(II) complexes, $1.45 \times 10^{-5} \text{ mol dm}^{-3}$ for Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)Iron(II) Sulphate at 500nm and $1.80 \times 10^{-5} \text{ mol dm}^{-3}$ for Tris-(4,7-dimethyl-1,10-

phenanthroline)Iron(II) Perchlorate at 510nm and the concentration of sodium dodecyl sulphate(SDS) was fixed at $2.00 \times 10^{-4} \text{ mol dm}^{-3}$. The effect of substrates like H^+ , OH^- , $\text{C}_6\text{H}_5\text{COONa}$ and urea at fixed concentrations were studied. Activation energies (E_a) were calculated from the Arrhenius equation from the plot of $\ln k_{\text{obs}}$ versus $1/T$ (K^{-1}) (figs. I&II). While activation parameters like ΔG^\ddagger , ΔS^\ddagger , ΔH^\ddagger as shown in Table V were calculated using Eyring's equation (Shoemaker, 2006).

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\ln \frac{k}{T} = - \frac{\Delta H^\ddagger}{RT} + \ln \frac{K}{h} + \frac{\Delta S^\ddagger}{R}$$

$$\ln \frac{K}{h} = 23.76$$

k = rate constant

T = Temperature

ΔH^\ddagger = Enthalpy of activation (Jmol^{-1})

ΔS^\ddagger = Entropy of activation (Jmol^{-1})

R = Molar gas constant

K = Boltzmann constant

Results and discussion

The dissociation constants were calculated from experimental data of binding constants and rate constant of binding. The higher rate of dissociation of $\text{SDS-Fe}(\text{Me}_4\text{phen})_3^{2+}$ bound substrate in OH^- compared with the bound $\text{SDS-Fe}(\text{Me}_2\text{phen})_3^{2+}$ as shown in Tables I(a&b) respectively implies that $\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$ is better stabilized with respect to dissociation due to the weaker hydrophobic/electrostatic interaction between SDS and $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$. This is consistent with a reduction in the hydrophobicity of the medium by OH^- . There is a stronger binding of $\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$ by SDS resulting from the higher electrostatic attraction between SDS and $\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$ as explained earlier. This trend quantitatively explain the same for the binding studies of H^+ (Table II(a&b), PhCOONa (Table III(a&b)) and urea (Table IV(a&b)). Generally for all the substrates, dissociation constant decreased with increased surfactant concentration. This implies that the higher the concentration of the surfactant the greater the binding which incidentally translates to higher binding constant.

The rate constant of dissociation is a function of the strength of binding between SDS and the Iron(II) complexes. The greater the binding constant the lower the rate constant of dissociation and vice-versa or the more stabilized the complex is with respect to dissociation. The rate of dissociation decreases generally with increase in the concentration of sodium dodecyl sulphate (SDS) in all the substrates (OH^- , H^+ , Benzoate ion and urea). This implies that the higher the SDS molecules the greater the binding force (coulombic/hydrophobic) between the surfactant and the Fe^{2+} complexes. Thereby resulting general decrease in dissociation of $\text{SDS-Fe}(\text{Me}_4\text{phen})_3^{2+}$ and $\text{SDS-Fe}(\text{Me}_2\text{phen})_3^{2+}$ complexes as the surfactant concentration increases. Moreover, rate of dissociation is greater in $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$ than $\text{SDS-Fe}(\text{Me}_2\text{phen})_3^{2+}$ in all the substrates. This implies that binding is more effective in $\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$ than $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$. This shows that dissociation is pronounced in bulky $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$ than less bulky $\text{Fe}(\text{Me}_2\text{phen})_3^{2+}$ which indicates the effect of steric hindrance on binding. The effect of substrates on rate of dissociation of $\text{SDS-Fe}(\text{Me}_4\text{phen})_3^{2+}$ was in the order:

Table 1a. Rate constant of dissociation of SDS- Fe(Me₄phen)₃²⁺ in OH⁻

	$k_{\text{diss}}/10^{-9}(\text{s}^{-1})$					
[SDS]/ 10 ⁻⁴ (M)	[OH ⁻] 0.50 x 10 ⁻⁵ M	[OH ⁻] 1.00 x 10 ⁻⁵ M	[OH ⁻] 1.50 x 10 ⁻⁵ M	[OH ⁻] 2.00 x 10 ⁻⁵ M	[OH ⁻] 2.50 x 10 ⁻⁵ M	[OH ⁻] 3.00 x 10 ⁻⁵ M
2.00	8.05	7.87	7.45	8.14	8.00	7.53
3.00	7.60	7.35	6.46	7.07	7.20	7.12
4.00	6.75	6.54	6.29	6.76	7.00	6.86
5.00	6.10	6.35	6.28	6.63	6.70	6.71
6.00	5.63	6.23	6.01	6.40	6.52	6.66
7.00	5.34	5.79	5.75	6.24	6.26	6.41
8.00	5.23	5.74	5.63	6.06	6.13	2.20

Table 1b. Rate constant of dissociation of SDS-Fe(Me₂phen)₃²⁺ in OH⁻

	$k_{\text{diss}}/10^{-9}(\text{s}^{-1})$					
[SDS]/10 ⁴ (M)	[OH ⁻] 0.50 x 10 ⁻⁵ M	[OH ⁻] 1.00 x 10 ⁻⁵ M	[OH ⁻] 1.50 x 10 ⁻⁵ M	[OH ⁻] 2.00 x 10 ⁻⁵ M	[OH ⁻] 2.50 x 10 ⁻⁵ M	[OH ⁻] 3.00 x 10 ⁻⁵ M
2.00	2.34	2.44	2.54	2.30	2.43	2.44
3.00	2.07	2.14	2.25	2.11	2.12	2.05
4.00	1.79	1.93	1.91	1.96	1.97	1.86
5.00	1.63	1.57	1.56	1.39	1.41	1.48
6.00	1.45	1.31	1.37	1.18	1.17	1.21
7.00	1.36	1.19	1.29	1.10	1.10	1.09
8.00	1.26	1.11	1.10	0.95	0.97	0.92

Table 2a. Rate constant of dissociation of SDS- Fe(Me₄phen)₃²⁺ in [H⁺]

	$k_{\text{diss}}/10^{-8}(\text{s}^{-1})$					
[SDS]/10 ⁻⁴ (M)	[H ⁺] 0.50 x 10 ⁻⁴ M	[H ⁺] 1.00 x 10 ⁻⁴ M	[H ⁺] 1.50 x 10 ⁻⁴ M	[H ⁺] 2.00 x 10 ⁻⁴ M	[H ⁺] 2.50 x 10 ⁻⁴ M	[H ⁺] 3.00 x 10 ⁻⁴ M
1.5	4.77	4.68	2.84	3.34	3.19	2.88
2.5	4.26	4.18	2.50	2.79	2.99	2.80
3.5	4.26	3.85	2.42	2.63	2.91	2.73
5.0	4.26	3.68	2.11	2.44	2.63	2.58
6.0	4.26	3.68	2.11	2.31	2.56	2.08
8.0	4.26	3.68	2.11	2.11	2.56	2.08

Table 2b. Rate constant of dissociation of SDS-Fe(Me₂phen)₃²⁺ in [H⁺]

	$k_{\text{diss}}/10^{-9}(\text{s}^{-1})$					
[SDS]/ 10 ⁻⁴ (M)	[H ⁺] 0.50 x 10 ⁻⁴ M	[H ⁺] 1.00 x 10 ⁻⁴ M	[H ⁺] 1.50 x 10 ⁻⁴ M	[H ⁺] 2.00 x 10 ⁻⁴ M	[H ⁺] 2.50 x 10 ⁻⁴ M	[H ⁺] 3.00 x 10 ⁻⁴ M
2.00	8.65	7.07	9.95	5.84	7.06	6.83
3.00	5.38	4.92	6.67	4.05	4.04	3.82
4.00	3.96	3.89	3.96	2.57	3.25	2.76
5.00	3.07	2.53	2.50	1.86	2.18	2.09
6.00	1.61	2.01	2.00	1.63	1.67	1.79
7.00	1.32	1.40	1.80	1.43	1.60	1.77
8.00	1.32	1.32	1.78	1.41	1.55	1.63

Table 3a. Rate constant of dissociation of SDS-Fe(Me₄phen)₃²⁺ in benzoate ion.

	$k_{\text{diss}}/10^{-9}(\text{s}^{-1})$					
[SDS]/ 10 ⁻⁴ (M)	[C ₆ H ₅ COONa] 0.50 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 1.00 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 1.50 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 2.00 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 2.50 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 3.00 x 10 ⁻⁵ M
2.00	5.65	6.55	6.61	6.37	7.02	3.44
3.00	5.45	5.75	6.01	5.52	5.63	2.83
4.00	5.19	4.96	5.36	4.81	4.75	2.53
5.00	5.12	4.87	4.93	4.45	4.56	2.26
6.00	4.69	4.64	4.70	4.34	4.30	2.22
7.00	4.87	4.44	4.49	4.14	4.19	2.10
8.00	4.84	4.33	4.36	3.90	4.00	1.97

Table 3b. Rate constant of dissociation of SDS-Fe(Me₂phen)₃²⁺ in benzoate ion

	$k_{\text{diss}}/10^{-9}(\text{s}^{-1})$					
[SDS]/ 10 ⁻⁴ (M)	[C ₆ H ₅ COONa] 0.50 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 1.00 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 1.50 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 2.00 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 2.50 x 10 ⁻⁵ M	[C ₆ H ₅ COONa] 3.00 x 10 ⁻⁵ M
2.00	2.43	2.64	2.70	2.89	2.80	2.79
3.00	1.81	2.17	2.25	2.48	2.42	2.61
4.00	1.13	1.33	1.33	1.36	1.37	1.52
5.00	1.08	1.09	1.11	1.17	1.21	1.23
6.00	0.87	0.98	1.03	1.04	1.10	1.00
7.00	0.84	0.91	0.93	0.95	0.94	0.93
8.00	0.83	0.85	0.88	0.90	0.91	0.89

Table 4a. Rate constant of dissociation of SDS-Fe(Me₄phen)₃²⁺ in urea

[SDS]/10 ⁻⁴ (M)	k _{diss} /10 ⁻⁹ (s ⁻¹)					
	[urea] 0.50 x 10 ⁻⁵ M	[urea] 1.00 x 10 ⁻⁵ M	[urea] 1.50 x 10 ⁻⁵ M	[urea] 2.00 x 10 ⁻⁵ M	[urea] 2.50 x 10 ⁻⁵ M	[urea] 3.00 x 10 ⁻⁵ M
2.00	10.6	9.86	8.59	8.40	8.06	7.91
3.00	8.78	9.35	8.36	7.74	6.67	6.64
4.00	8.33	8.13	7.81	6.54	6.39	6.36
5.00	7.88	7.41	7.29	6.40	5.98	6.08
6.00	7.24	6.47	6.38	6.14	5.83	5.93
7.00	6.41	5.99	5.73	5.60	5.56	5.65
8.00	5.77	5.52	5.47	5.34	5.42	5.51

Table 4b. Rate constant of dissociation of SDS-Fe(Me₂phen)₃²⁺ in urea

[SDS]/10 ⁻⁴ (M)	k _{diss} /10 ⁻⁹ (s ⁻¹)					
	[urea] 0.50 x 10 ⁻⁵ M	[urea] 1.00 x 10 ⁻⁵ M	[urea] 1.50 x 10 ⁻⁵ M	[urea] 2.00 x 10 ⁻⁵ M	[urea] 2.50 x 10 ⁻⁵ M	[urea] 3.00 x 10 ⁻⁵ M
2.00	3.76	3.75	3.57	3.24	4.60	7.85
3.00	3.31	3.64	3.46	2.80	3.08	4.25
4.00	2.66	2.71	2.57	2.05	2.27	3.04
5.00	1.99	2.11	1.99	1.56	1.57	1.54
6.00	1.80	1.82	1.82	1.54	1.55	1.50
7.00	1.61	1.74	1.67	1.50	1.53	1.48
8.00	1.47	1.72	1.64	1.34	1.52	1.48

Table 5. Activation parameters of binding of the two complexes with SDS

Substrate	E _a (kJmol ⁻¹)		ΔH [‡] (kJmol ⁻¹)		ΔS [‡] (kJK ⁻¹ mol ⁻¹)		ΔG [‡] (kJmol ⁻¹)	
	Fe(Me ₄ phen) ₃ ²⁺	Fe(Me ₂ phen) ₃ ²⁺	Fe (Me ₄ phen) ₃ ²⁺	Fe (Me ₂ phen) ₃ ²⁺	Fe (Me ₄ phen) ₃ ²⁺	Fe (Me ₂ phen) ₃ ²⁺	Fe (Me ₄ phen) ₃ ²⁺	Fe (Me ₂ phen) ₃ ²⁺
–	39.96	23.88	37.48	21.40	-9.69	-10.15	58.23	55.91
Urea	30.28	25.57	27.80	23.09	-10.02	-10.09	58.77	55.48
Benzoate ion	16.46	16.26	13.98	13.78	-10.13	-10.35	57.29	54.19
OH ⁻	33.69	20.92	31.21	18.44	-9.91	-10.21	58.94	54.94
H ⁺	26.82	18.86	24.34	16.38	-10.11	-10.32	57.43	56.00

Benzoate ion < OH⁻ < Urea < H⁺. while in SDS-Fe(Me₂phen)₃²⁺, it was in the order: OH⁻ < benzoate ion < H⁺ < urea. Dissociation is low in benzoate ion because of the unique orientation which shows that the phenyl group of the benzoate ion aligns itself below the head group of SDS monomers due to its hydrophobic nature. Hence 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, thereby leading to strong binding. Furthermore, dissociation is great in urea owing to the fact that urea reduces the negative charge density on the surfactant which leads to weak binding.

The activation parameters (E_a, ΔG[‡], ΔS[‡] and ΔH[‡]) are lower for Fe(Me₂phen)₃²⁺ than Fe(Me₄phen)₃²⁺. This accounted for the general increase in rate constant of binding for Fe(Me₂phen)₃²⁺ than Fe(Me₄phen)₃²⁺. The low values of activation energies obtained for benzoate ion dependent studies for both Iron(II) complexes shows that the rate of binding was highest in the benzoate ion compared to all other substrates. In Fe(Me₄phen)₃²⁺, the activation energy was in the order: benzoate ion < H⁺ < urea < OH⁻ < neutral. while in Fe(Me₂phen)₃²⁺ there was a slight shift in the corresponding order: benzoate < H⁺ < OH⁻ < neutral < urea. The observed slight invariance in the free energy of activation suggest the same mechanism for the binding process as enhanced by the compensating effects of enthalpy and entropy of activation. Negative values of ΔS[‡] obtained for both complexes indicated that the formation of the activated

complex from the reactants was accompanied by a large decrease in entropy which often indicate an association mechanism (Espenson, 1981).

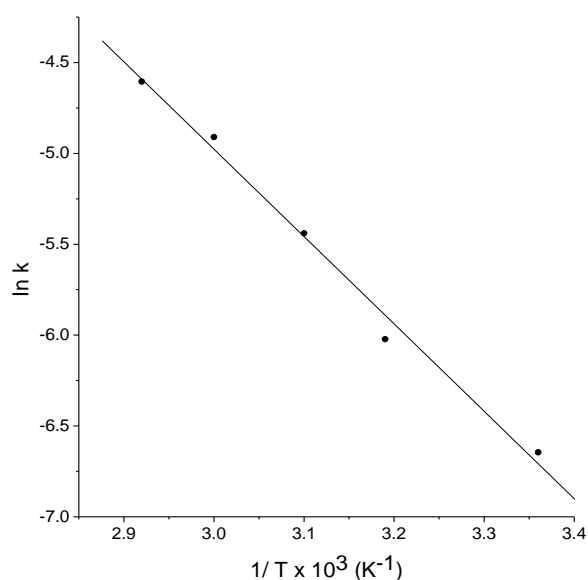


Figure 1. Plot of ln k versus 1/T (K⁻¹) for binding between SDS and Fe(Me₄phen)₃²⁺/Fe(Me₂phen)₃²⁺] 1.45 x 10⁻⁵ mol dm⁻³, 25 ≤ T^oC ≤ 70, [SDS] 2.00 x 10⁻⁴ mol dm⁻³

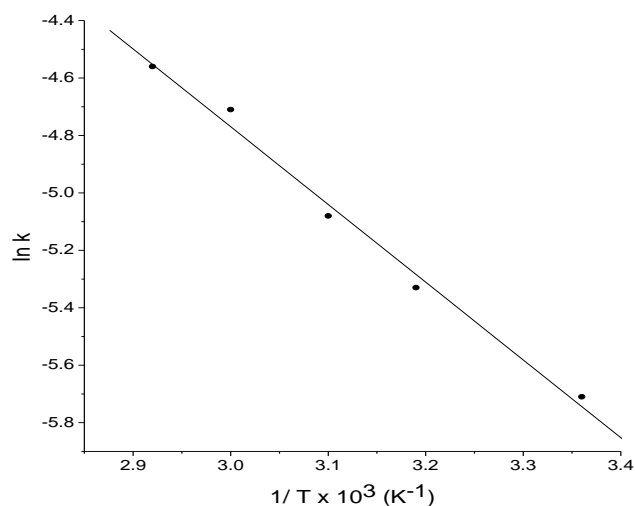


Figure 2. Plot of $\ln k$ versus $1/T$ (K^{-1}) for binding between SDS and $Fe(Me_2phen)_3^{2+}$ [$Fe(Me_2phen)_3^{2+}$] $1.80 \times 10^{-5} \text{ mol dm}^{-3}$, $25 \leq T^\circ C \leq 70$, [SDS] $2.00 \times 10^{-4} \text{ mol dm}^{-3}$

Conclusion

Sodium dodecyl sulphate binds readily onto $Fe(Me_2phen)_3^{2+}$ than $Fe(Me_4phen)_3^{2+}$ in all the substrates. Binding was most enhanced in benzoate ion compared to other substrates. Moreover, both hydrophobic and electrostatic forces played vital role in the binding and dissociation of SDS-Fe(II) complexes.

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