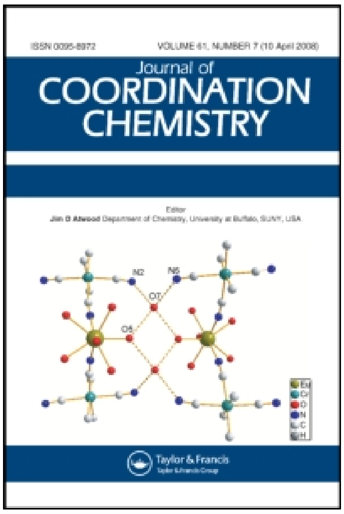

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SPECTROPHOTOMETRIC INVESTIGATION OF THE REACTIONS OF TETRAKIS(1,10-PHENANTHROLINE)-DIAQUO-μ-OXODIIRON(III) WITH SALICYLIC AND SULFOSALICYLIC ACIDS

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Reactions of the binuclear oxo-bridged complex tetrakis(1,10-phenanthroline)diaquo-μ-oxodiiron(III), $[(\text{phen})_2(\text{H}_2\text{O})\text{-Fe–O–Fe}(\text{H}_2\text{O})(\text{phen})_2]^{4+}$, with salicylic or sulfosalicylic acid were investigated spectrophotometrically in the pH range 2.0–9.0 in aqueous medium. Salicylate (Sa^{2-}) and sulfosalicylate (Su^{3-}) form complexes $\text{Fe(phen)}_2\text{Sa}^+$ and $\text{Fe(phen)}_2\text{Su}$, respectively, in the pH range 2.0–3.5, and Fe(phen)Sa_2^- and Fe(phen)Su_2^{3-}, respectively, in the pH range 7.0–9.0. The mono-phenanthroline and the bis-phenanthroline complexes coexist in equilibrium in the pH range 3.5–7.0. The salicylate complexes exhibit an isosbestic point at 563 nm, and the sulfosalicylate complexes show the isosbestic point at 565 nm. The complexes $\text{Fe(phen)}_2\text{Sa}^+$ and Fe(phen)Sa_2^- have λ_{max} at 520 nm ($\epsilon = 2.19 \times 10^3$ l mole^{-1} cm^{-1}) and 490 nm ($\epsilon = 4.06 \times 10^3$ l mole^{-1} cm^{-1}), respectively, while the corresponding values for the complexes $\text{Fe(phen)}_2\text{Su}$ and Fe(phen)Su_2^{3-} are 510 nm ($\epsilon = 2.55 \times 10^3$ l mole^{-1} cm^{-1}) and 480 nm ($\epsilon = 4.53 \times 10^3$ l mole^{-1} cm^{-1}), respectively. The formation constants for these complexes are:

$$\frac{[\text{Fe(phen)}_2\text{Sa}^+]}{[\text{D}]^{0.5}[\text{Sa}^{2-}][\text{H}^+]} = 6.25 \times 10^{15}$$

$$\frac{[\text{Fe(phen)(Sa)}_2^-][\text{Phen}]}{[\text{Fe(phen)}_2\text{Sa}^+][\text{Sa}^{2-}]} = 4.85 \times 10^{7}$$

$$\frac{[\text{Fe(phen)}_2\text{Su}]}{[\text{D}]^{0.5}[\text{Su}^{3-}][\text{H}^+]} = 6.02 \times 10^{13}$$

$$\frac{[\text{Fe(phen)(Su)}_2{}^{3-}][\text{phen}]}{[\text{Fe(phen)}_2\text{Su}][\text{Su}^{3-}]} = 2.77 \times 10^{4}$$

where D represents $(\text{phen})_2(\text{H}_2\text{O})\text{Fe–O–Fe}(\text{H}_2\text{O})(\text{phen})_2{}^{4+}$.

INTRODUCTION

Iron(III) salts are known to form complexes of varying composition with phenols and hydroxybenzoic acids.[1-8] Among them salicyclic acid (o-hydroxybenzoic acid) and sulfosalicylic acid (2-hydroxy-5-sulfobenzoic acid) have undergone detailed investigation.[1-4,7,8] Salicylic and sulfosalicylic acids form violet colored complexes in solution of pH below 3.0 while the color shifts over orange to yellow with increase in pH. The violet color is due to the formation of a complex in which the iron(III) to ligand ratio is 1:1 which is converted to the 1:2 and 1:3 complexes with the increase in pH. The equilibrium constants for the formation of these complexes have been determined.[1-4,7]

The present work deals with the color reactions of salicylic or sulfosalicylic acid with tetrakis-(1,10-phenanthroline)diaquo-μ-oxodiiron(III), $(\text{phen})_2(\text{H}_2\text{O})\text{Fe–O–Fe}(\text{H}_2\text{O})(\text{phen})_2^{4+}$ (hereafter referred to as "D"), in aqueous medium. Violet color formed at low pH changes to pink at higher pH. Spectrophotometric study reveals the formation of two mixed ligand complexes of iron(III) with varying composition of 1,10-phenanthroline and salicylate or sulfosalicylate. Stability constants for the formation of these complexes are also presented.

EXPERIMENTAL

Reagents

Tetrakis(1,10-phenanthroline)-μ-oxodiiron(III) chloride, $[(phen)_2(Cl)Fe-O-Fe(Cl)(phen)_2]Cl_2$, was prepared by the published procedure.[9,10] Solutions of salicylic acid or sulfosalicylic acid were prepared by dissolving reagent grade products (Aldrich) in distilled water. Sodium acetate-acetic acid buffers were prepared by mixing appropriate volumes of 0.50 *M* acetic acid and 0.50 *M* sodium acetate to give the desired pH value, the pH being monitored by a pH meter.

Physical Measurements

The electronic absorption spectra and absorbance measurements were obtained on a Zeiss RPQ 20A recording spectrometer or a Beckman DU-2 spectrometer. pH measurements were effected with the aid of a Corning Model 7 pH-meter and a combination glass-calomel electrode (Corning 476050) which could be introduced directly into the 50 ml volumetric flask for pH mesaurements.

Procedure for Determining the Stability Constants

Concentration of aqueous solution of D employed in the present work was $6.25 \times 10^{-4} M$. Predetermined volumes of D (5.0 ml) and 0–10 ml of salicylic or sulfosalicylic acid ($6.25 \times 10^{-3} M$) were mixed in a series of 50 ml volumetric flasks, followed by 10.0 ml of the buffer solution of the required pH value. The whole solution was diluted to about 40 ml, and slight changes in pH, if necessary, was effected by adding 0.50 *M* sodium acetate or acetic acid by means of a graduated pipette. The whole solution was then diluted to 50 ml in the volumetric flask after the addition of a calculated volume of 1.0 *M* sodium perchlorate to adjust the total ionic strength to 0.20. The pH was maintained within ±0.05 of the required value by this procedure. The absorbance at the desired wavelength or the absorption curve over the range 400–650 nm was recorded (using a cell of suitable path-length) after two to three hours within which the solutions were found to reach equilibrium. The reactions were carried out at room temperature (24 ± 1 °C).

RESULTS AND DISCUSSION

In the pH range 2.0–3.5 aqueous solutions of D and sulfosalicylic acid formed a violet complex with absorption maximum at 510 nm. This λ_{max} shifted to shorter wavelengths with concomitant change of color from violet to pink when the pH was increased gradually to 7.0. An isosbestic point was observed at 565 nm in the pH range 3.5–7.0 indicative of the existence of two complexes at equilibrium. In the pH range 7.0–9.0 all the absorption curves were identical with an absorption maximum at 480 nm. At pH values above 9.0 the solutions developed turbidity with consequent destruction of the complex. Iron(III) salts and sulfosalicylic acid are known to change color from violet through orange to yellow and exhibit two isosbestic points at 549 (pH range 2–5) and 459 nm (pH range 5–9) indicative of the successive formation of three complexes.[1,3,4] But in the present study only two complexes were found to be in equilibrium.

Salicylic acid reacted with D in a manner similar to that of sulfosalicylic acid. The violet complex formed in the pH range 2.0–3.5 showed an absorption maximum at 520 nm. The color changed to pink with the increase in pH. An isosbestic point was observed at 563 nm in the pH range 3.5–7.0. Only the pink complex, which had an absorption maximum at 490 nm, existed in the pH range 7.0–9.0. The electronic absorption spectra of the complexes of D with salicylate and sulfosalicylate are included in Figure 1.

A continuous variation analysis (Job plot) indicated that two moles of salicylic or sulfosalicylic

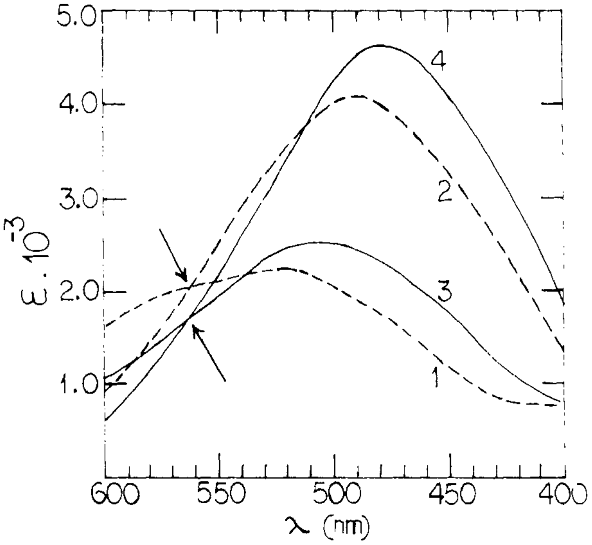

FIGURE 1 Electronic absorption spectra of the complexes, 1. $[Fe(phen)_2Sa]^+$; 2. $[Fe(phen)(Sa)_2]^-$; 3. $[Fe(phen)_2Su]$; and 4. $[Fe(phen)(Su)_2]^{3-}$ in aqueous media. The arrows indicate the isosbestic points.

acid reacted with one mole of D in the pH range 2.0–3.5, where only the violet complex exists, while four moles of salicylic or sulfosalicylic acid were required per mole of D in the pH range 7.0–9.0, where only the pink complex exists. The following reactions may summarise the observed changes.

$$\tfrac{1}{2}[(\text{phen})_2(H_2O)\text{Fe–O–Fe}(H_2O)(\text{phen})_2]^{4+} + \text{Sa}^{2-} + H^+ \rightleftharpoons [\text{Fe(Phen)}_2(\text{Sa})]^+ + 1\tfrac{1}{2}H_2O \quad (1)$$

$$[\text{Fe(phen)}_2\text{Sa}]^+ + \text{Sa}^{2-} \rightleftharpoons [\text{Fe(phen)(Sa)}_2]^- + \text{phen} \quad (2)$$

$$\tfrac{1}{2}[(\text{phen})_2(H_2O)\text{Fe–O–Fe}(H_2O)(\text{phen})_2]^{4+} + \text{Su}^{3-} + H^+ \rightleftharpoons [\text{Fe(phen)}_2\text{Su}] + 1\tfrac{1}{2}H_2O \quad (3)$$

$$[\text{Fe(phen)}_2\text{Su}] + \text{Su}^{3-} \rightleftharpoons [\text{Fe(phen)(Su)}_2]^{3-} + \text{phen} \quad (4)$$

where Sa^{2-} and Su^{3-} are salicylate dianion and sulfosalicylate trianion, respectively. Apparently, Sa^{2-} and Su^{3-} are incapable of displacing the remaining phen molecule to form a complex with iron(III) to Sa^{2-} or Su^{3-} ratio 1:3 as is normally observed in the reactions of iron(III) salts with salicylic or sulfosalicylic acids.[1,3,4]

The complex D is known to react with CN^-, a strong field lignad, effecting the substitution of H_2O and bridge O^{2-} to form $[\text{Fe(phen)}_2(CN)_2]^+$.[11] The thiocyanate ion, a ligand of medium strength, substitutes only the H_2O molecules in aqueous medium of pH 3.0–4.0, while H_2O and bridge O^{2-} are substituted by NCS^- ligands in the presence of added acid (pH 1.3–1.5).[12] It was suggested[12] that H^+ weakens the Fe–O–Fe bonds due to protonation at the bridge O^{2-}. In the present study, the best pH condition for the formation of the complexes $[\text{Fe(phen)}_2\text{Sa}]^+$ and $[\text{Fe(phen)}_2\text{Su}]$ was 3.0 ± 0.1. This means that a weakening of the Fe–O–Fe bridge bonds due to protonation may not be the one responsible for the reactions. It is probable that the chelate effect is a major factor responsible for the substitution of H_2O and bridge O^{2-} by Sa^{2-} and Su^{3-} observed in the present investigation.

The molar absorptivities for the complexes $[\text{Fe(phen)}_2\text{Sa}]^+$, $[\text{Fe(phen)}_2\text{Su}]$, $[\text{Fe(phen)(Sa)}_2]^-$ and $[\text{Fe(phen)(Su)}_2]^{3-}$ at the wavelength of their maximum absorption are included in Tables I and II. Since only the mono-phenanthroline complexes exist in the pH range 7.0–9.0, it is easy to determine the molar absorptivity values (ϵ_2) for these complexes at the wavelength of their maximum absorption (490 nm for the salicylate complex, and 480 nm for the sulfosalicylate complex) by measuring the abosrbances at the desired wavelength of the solutions containing varying concentrations of D (2.5×10^{-5} – $8.75 \times 10^{-5}M$) and high enough concentration of salicylic or sulfosalicylic acid ($1.25 \times 10^{-2}M$) to ensure complete reaction. Least square analysis was used to calculate ϵ_2. The isosbestic point method of McBryde et al was employed to calculate ϵ_1 values for the bis-phenanthroline complexes.[7]

TABLE I
Stability constants for salicylate complexes

pH	Φ	λ, nm	ϵ_0	ϵ_1	ϵ_2	log K_1	log K_2
3.00	4.84×10^{10}	520	160	2190	–	15.79 ± 0.02	–
5.80	3.96×10^{7}	490	–	1770	4060	–	7.68 ± 0.02

K_{s1} and K_{s2} values employed in the present calculations were 1.07×10^{-3} and 4.0×10^{-14}, respectively (ref. 7).

TABLE II
Stability constants for sulfosalicylate complexes

pH	Φ	λ, nm	ϵ_0	ϵ_1	ϵ_2	log K_1	log K_2
3.00	3.08×10^{8}	510	192	2550	–	13.78 ± 0.02	–
6.20	1.62×10^{5}	480	–	2370	4530	–	4.44 ± 0.02

K_{s1} and K_{s2} values employed in the present calculations were 5.05×10^{-3} and 3.89×10^{-12}, respectively (ref. 7).

The Stability Constants of the Complexes

According to the reactions (1)–(4), the equilibrium constants for the formation of the complexes may be written as:

$$K_1 = \frac{[\mathrm{Fe(phen)_2S}]}{[\mathrm{D}]^{0.5}[\mathrm{S}][\mathrm{H^+}]} \tag{5}$$

$$K_2 = \frac{[\mathrm{Fe(phen)S_2}][\mathrm{phen}]}{[\mathrm{Fe(phen)_2S}][\mathrm{S}]} \tag{6}$$

where S represents the salicylate or sulfosalicylate anion. For convenience the charges on the complexes have been omitted in the equilibrium equations.

Since only $\mathrm{Fe(phen)_2S}$ and D are in equilibrium at pH 3.5 and below,[10] and only $\mathrm{Fe(phen)_2S}$ and $\mathrm{Fe(phen)S_2}$ at pH values 3.5–7.0, the equations (5) and (6) may be treated independently to determine K_1 and K_2.

If D and $\mathrm{Fe(phen)_2S}$ are in equilibrium, the absorbance, A, at any desired wavelength is,

$$A = \epsilon_0[\mathrm{D}] + \epsilon_1[\mathrm{Fe(phen)_2S}] \tag{7}$$

where ϵ_0 is the molar absorptivity of D at the desired wavelength. The total analytical concentration of iron(III) in solution is

$$[\mathrm{Fe}] = 2[\mathrm{D}] + [\mathrm{Fe(phen)_2S}] \tag{8}$$

From equations (5), (7) and (8), and taking into account that $[\mathrm{S}] = ([\mathrm{S}]_t - [\mathrm{Fe(phen)_2S}])/\Phi$ we arrive at the following equation.

$$\frac{2A - \epsilon_0[\mathrm{Fe}]}{A - \epsilon_1[\mathrm{Fe}]} = -K_1 \quad \frac{[\mathrm{H^+}]([\mathrm{S}]_t - [\mathrm{Fe(phen)_2S}])}{[\mathrm{D}]^{0.5}\Phi} \tag{9}$$

where $[\mathrm{S}]_t$ is the total analytical concentration of salicylic or sulfosalicylic acid, $[\mathrm{Fe(phen)_2S}] = (2A - \epsilon_0[\mathrm{Fe}])/(2\epsilon_1 - \epsilon_0)$, $[\mathrm{D}] = (\epsilon_1[\mathrm{Fe}] - A)/(2\epsilon_1 - \epsilon_0)$, and $\Phi = 1 + ([\mathrm{H^+}]/K_{s2}) + ([\mathrm{H^+}]^2/K_{s1}K_{s2})$, K_{s1} and K_{s2} being the first and second acid dissociation constants for salicylic or sulfosalicylic acid.[13]

In order to determine K_1, the absorbances at the wavelength maximum (510 nm for sulfosalicylic acid complex and 520 nm for salicylic acid complex) were determined at constant initial concentration of D ($6.25 \times 10^{-5} M$) and varying concentrations of S_t ($1.25 \times 10^{-4} - 6.25 \times 10^{-4} M$) at constant pH 3.0 and total ionic strength of 0.20. K_1 is determined as the slope of the plot of $[\mathrm{H^+}]([\mathrm{S}]_t - [\mathrm{Fe(phen)_2S}])/[\mathrm{D}]^{0.5}\Phi$ *vs* $(2A - \epsilon_0[\mathrm{Fe}])/(A - \epsilon_1[\mathrm{Fe}])$.

If conditions are such that only $\mathrm{Fe(phen)_2S}$ and $\mathrm{Fe(phen)S_2}$ are in equilibrium (pH 3.5–7.0), the absorbance may be written as,

$$A = \epsilon_1[\mathrm{Fe(phen)_2S}] + \epsilon_2[\mathrm{Fe(phen)S_2}] \tag{10}$$

The total analytical concentration of iron(III) is,

$$[\mathrm{Fe}] = [\mathrm{Fe(phen)_2S}] + [\mathrm{Fe(phen)S_2}] \tag{11}$$

From equations (6), (10) and (11), and taking into account that $[\mathrm{S}] = \{[\mathrm{S}]_t - ([\mathrm{Fe}] + [\mathrm{Fe(phen)S_2}])\}/\Phi$ and $[\mathrm{phen}] = [\mathrm{Fe(phen)S_2}]$, we arrive at equation (12).

$$\frac{A - \epsilon_1[\mathrm{Fe}]}{A - \epsilon_2[\mathrm{Fe}]} = -K_2 \quad \frac{[\mathrm{S}]_t - ([\mathrm{Fe}] + [\mathrm{Fe(phen)S_2}])}{[\mathrm{Fe(phen)S_2}]\Phi} \tag{12}$$

where, $[\mathrm{Fe(phen)S_2}] = (A - \epsilon_1[\mathrm{Fe}])/(\epsilon_2 - \epsilon_1)$.

In order to determine K_2, the absorbances at the wavelength of maximum absorbance (490 nm for salicylate complexes and 480 nm for sulfosalicylate complexes) were determined at constant initial concentration of D ($6.25 \times 10^{-5} M$) and varying concentrations of S_t ($7.5 \times 10^{-4} - 2.0 \times 10^{-3} M$) at constant ionic strength of 0.20 and constant pH (5.80 for salicylic acid and 6.20 for sulfosalicylic acid). K_2 was obtained as the slope of the plot of $\{[\mathrm{S}]_t - ([\mathrm{Fe}] + [\mathrm{Fe(phen)S_2}])\}/[\mathrm{Fe(phen)S_2}]\Phi$ *vs* $(A - \epsilon_1[\mathrm{Fe}])/(A - \epsilon_2[\mathrm{Fe}])$. The results are included in Tables I and II.

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10. In aqueous medium this complex undergoes aquation to $[(\text{phen})_2(H_2O)Fe{-}O{-}Fe(H_2O)(\text{phen})_2]^{4+}$ which acts as a dibasic acid ($pK_{D1} = 4.3$; $pK_{D2} = 6.4$) to form $[(\text{phen})_2(OH)Fe{-}O{-}Fe(OH_2)(\text{phen})_2]^{3+}$ and $[(\text{phen})_2(OH)Fe{-}O{-}Fe(OH)(\text{phen})_2]^{2+}$. Under the conditions at which K_1 is determined (pH = 3.0 and $[D] = 6.25 \times 10^{-4} M$) the concentration of the dihydroxy species is less than 0.01% while the concentration of the monohydroxy species is less than 5.0%.
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