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# Study of Equilibria and Kinetics of the Interactions of Iron(III) with 8-Hydroxyquinoline and 8-Hydroxyquinoline-5-sulfonic Acid in $HClO_4$-$NaClO_4$ Media

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The equilibria and kinetics of the reaction of iron(III) with 8-hydroxyquinoline (oxine) and 8-hydroxyquinoline-5-sulfonic acid under the condition of 1 : 1 chelate formation at different temperatures (35—45 °C) and ionic strength $I$=1.0 mol dm$^{-3}$ ($NaClO_4$+$HClO_4$) have been studied. A dual path mechanism involving both $Fe^{3+}_{aq}$ and $Fe(OH)^{2+}_{aq}$ species and the undissociated ligand ($LH_2^+$, $LH_2^{\pm}$) is consistent with the experimental observations under the experimental condition. The different rate constants have been deternined from the attainment of the equilibrium from both directions i.e., from the study of complex formation at low acid concentration and from the study of decomposition of the complex in presence of higher acid concentration. The results obtained from the both studies are found comparable within the experimental error limit. The results conform to $k_{obsd}/B=k_1[H^+]+k_2K_h$ where,

$$B=\frac{T_{Fe}}{[H^+]+K_h}+\frac{[H^+]}{Q};$$ $K_h$=hydrolysis constant of $Fe^{3+}_{aq}$, $k_1$ and $k_2$ are the forward second order rate constants of $Fe^{3+}_{aq}$ and $Fe(OH)^{2+}_{aq}$ respectively and $Q$ is the equilibrium constant of the reaction, $Fe^{3+}+LH_2^+ \rightleftarrows FeL^{2+}+2H^+$ where $LH_2^+$ represents the protonated form of the ligand, 8-hydroxyquinoline and a similar reaction occurs for 8-hydroxyquinoline-5-sulfonic acid ($LH_2^{\pm}$). Thermodynamic parameters for each of the steps have been determined. The results are compared with those of recent findings in the interaction of cerium(IV) with these ligands in perchloric acid media. $Fe(OH)^{2+}_{aq}$ appears to react through a purely dissociative fashion (Eigen–Tamm mechanism) and its characteristic water exchange rate has been found, as a rough estimate. On the other hand $Fe^{3+}_{aq}$ appears to react through the associative interchange ($I_a$) mechanism. The equilibrium constants ($Q$) obtained spectrophotometrically have been compared with those obtained from kinetic studies.

The mechanism of formation of labile metal complexes of divalent cations of the 1st transition series is well documented[1] and according to Eigen–Mechanism[2] the rate is determined by the rate of water exchange at the inner coordination sphere of the metal.

However in the case of 1st row trivalent transition metal ions, specially for Fe(III) no such clear cut mechanism has been established. Because of its strong propensity to hydrolyze[3,4] even in a moderately acidic solution to $Fe(OH)^{2+}_{aq}$ which can undergo dimerization,[5,6] the number of possible active species increases and it makes the mechanistic interpretation complicated. In $Fe(OH)^{2+}_{aq}$ the presence of OH increases[7] the rate of water exchange by a factor about three and gives a dissociative character[8] at the metal center. The enhanced reactivity of the hydrolyzed form depresses the relative importance of the unhydrolyzed species $Fe^{3+}_{aq}$. In the reactions with mandelic acid,[9] tiron,[10] 2,7-dichlorochromotropic acid,[10] citric acid,[11] tartaric acid,[11] *o*-aminophenol,[12] and (2-hydroxymethyl)-phenol[13] only $Fe(OH)^{2+}_{aq}$ has been found to be reactive. There are some cases such as salicylates,[14] hydroxamic acids,[15] phenols,[12] salicylaldehyde,[16] and *o*-hydroxyacetophenone[16] where both $Fe^{3+}_{aq}$ and $Fe(OH)^{2+}_{aq}$ have been found to be reactive. But there is no case yet reported where $Fe^{3+}_{aq}$ is found to be the only reactive species. As a matter of fact, though the kinetic behavior of $Fe(OH)^{2+}_{aq}$ is more or less well established but very few kinetic data on the unhydrolyzed species $Fe^{3+}_{aq}$ are available and its behavior is still an object of conjecture. Therefore, the ligands, 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid differing in basicity have been considered.

Very recently, the kinetics of mono-complex formation in the reaction of cerium(IV) with the present ligands have been studied[17] in acidic media. Hence the present study furnishes a worthy comparison between a f-block element and a d-block element although they differ in charge. However, such a comparison of different kinetic parameters is rare in literature.

Here it is important to mention that in many cases so far studied, due to the proton ambiguity, the reaction path, $Fe(OH)^{2+}_{aq}$+$LH_2^+$ cannot be kinetically distinguished from $Fe^{3+}$+LH. In such cases, it is necessary to choose between the alternatives by examining the reasonableness[18] of the rate constants obtained. In the present cases, the ligands were chosen in such a way so that they remain solely in the protonated form $LH_2^+$ or $LH_2^{\pm}$ and the kinetic contribution from the species LH (charges are omitted) becomes negligible, and thus no proton ambiguity arises. Here it is worth mentioning that a preliminary report without any details on the kinetics of iron(III) with 8-hydroxyquinoline is avail-

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able[19] in literature. The present investigation was undertaken to establish the thermodynamic aspects of the equilibria and different kinetic paths with their activation parameters from the analysis of the attainment of the equlibrium from both directions i.e., from the complex formation study (at lower acid concentration) and acid promoted (at higher acid concentration) decomplexation study.

## Experimental

**Reagents and Materials:** Standard stock solutions of Fe(III) perchlorate in perchloric acid media, sodium perchlorate and perchloric acid were prepared as described[15] earlier. The ligands (AR grade) were recrystallized and weighed amounts were taken to prepare the solutions. Freshly prepared ligand solutions were used in the study. Doubly distilled water was used to prepare all the solutions.

**Apparatus and Procedure:** The spectra of the freshly prepared complexes in solution were recorded using a Carl-Zeiss Spectrophotometer (VSU-2P, Jena, Germany) for equilibrium study. The kinetic measurements were done in a stopped-flow spectrophotometer (SF-3A, Hi-Tech, UK) coupled with an oscilloscope (Advance Instruments OS1000A) and a microprocessor with the help of which the pseudo first order rate constants were calculated. The flow module of the SF-3A had arrangements for thermostatting (±0.05 °C) the reacting solutions and the observation cell of the flow module. Ionic strength was adjusted to 1.0 mol dm$^{-3}$ with an adequate amount of NaClO$_4$ in addition to HClO$_4$ present in solution.

## Results and Discussion

**(a) Spectrophotometric Equilibrium Study:** A spectral study for the both ligands shows that at a fixed [HClO$_4$] and ligand concentration, the absorbance at the corresponding $\lambda_{\max}$ (645 and 625 nm for 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid respectively) increases with the increase of total iron concentration, $T_{\mathrm{Fe}}$ (in each case, $T_{\mathrm{Fe}}$ was at least 10 times the ligand concentration to assure the formation of mono-complex). This suggests that the systems are in equilibrium. In the experimental condition, [H$^+$]= 0.15 mol dm$^{-3}$ and temperature range (35—45 °C) the major reactant species are $\mathrm{Fe(H_2O)_6^{3+}}$ (the hydrolysis constants,[20] $K_h$ for the reaction, $\mathrm{Fe^{3+}+H_2O \rightleftarrows Fe(OH)^{2+}+H^+}$ at $I$=1.0 mol dm$^{-3}$, at 35 °C, 40 °C, and 45 °C are 2.95×10$^{-3}$, 3.84×10$^{-3}$, and 4.9×10$^{-3}$ respectively) and the protonated ligand $\mathrm{LH_2^{+/\pm}}$ (the p$K_a$ values[21] for the deprotonation processes, $\mathrm{LH_2^{+/\pm} \rightleftarrows LH^{0/1-}+H^+}$, $\mathrm{LH^{0/1-} \rightleftarrows L^{1-/2-}+H^+}$ for 8-hydroxyquinoline ($\mathrm{LH_2^+}$) are 4.83 and 9.50 at 35 °C at $I$=0.1 mol dm$^{-3}$ while the corresponding values for 8-hydroxyquinoline-

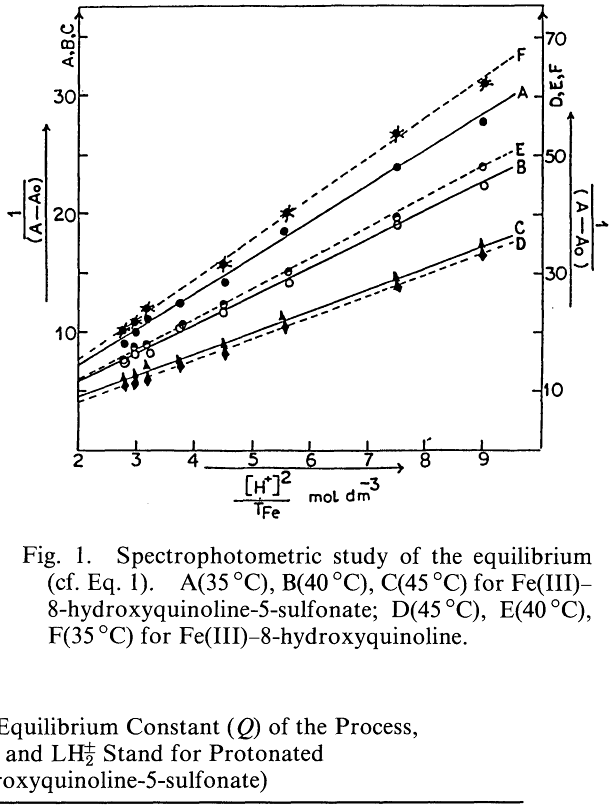

Fig. 1. Spectrophotometric study of the equilibrium (cf. Eq. 1). A(35 °C), B(40 °C), C(45 °C) for Fe(III)–8-hydroxyquinoline-5-sulfonate; D(45 °C), E(40 °C), F(35 °C) for Fe(III)–8-hydroxyquinoline.

Table 1. Thermodynamic Parameters of the Equilibrium Constant ($Q$) of the Process, $\mathrm{Fe^{3+}+LH_2^{+/\pm} \rightleftarrows FeL^{2+/1+}+2H^+}$ ($\mathrm{LH_2^+}$ and $\mathrm{LH_2^\pm}$ Stand for Protonated 8-Hydroxyquinoline and 8-Hydroxyquinoline-5-sulfonate)

| Method of measurement | 10$^2Q$/mol dm$^{-3}$, for 8-hydroxyquinoline system | | | | 10$^2Q$/mol dm$^{-3}$, for 8-hydroxyquinoline-5-sulfonic acid system | | | |
|---|---|---|---|---|---|---|---|---|
| | 25 °C | 35 °C | 40 °C | 45 °C | 25 °C | 35 °C | 40 °C | 45 °C |
| Spectrophotometric study | | 10.50<br>±0.40 | 14.20<br>±0.30 | 19.60<br>±0.80 | | 18.40<br>±0.50 | 23.10<br>±0.60 | 31.00<br>±0.70 |
| Kinetic study | | 11.50<br>±0.50 | 14.80<br>±0.50 | 18.40<br>±0.70 | | 17.60<br>±0.30 | 23.90<br>±0.50 | 30.40<br>±0.80 |
| Average value | 6.13$^{a)}$<br>1.9$^{b)}$ | 11.00<br>±0.45 | 14.50<br>±0.40 | 19.00<br>±0.70 | 10.12$^{a)}$<br>17.78$^{b)}$ | 18.00<br>±0.40 | 23.50<br>±0.55 | 30.70<br>±0.75 |
| $\Delta H^{c)}$ (kJ mol$^{-1}$) | 44.65±2.20 | | | | 43.95±2.52 | | | |
| $\Delta S^{c)}$ (J K$^{-1}$ mol$^{-1}$) | 126.51±7.56 | | | | 128.31±10.03 | | | |

a) Calculated values from the experimental results. b) Values obtained by using the values[21] of $\beta_1$ and p$K_a$'s of the ligands by using the relation, $Q=\beta_1 K_{a(1)} K_{a(2)}$. For $\mathrm{LH_2^+}$, $\log\beta_1$=13.0, p$K_{a(1)}$=5.09, p$K_{a(2)}$=9.62 at 25 °C, $I$=0.5 mol dm$^{-3}$. For $\mathrm{LH_2^\pm}$, $\log\beta_1$=11.6, p$K_{a(1)}$=3.93 and p$K_{a(2)}$=8.42, at 25 °C, $I$=0.1 mol dm$^{-3}$. c) Computed by using the average values of $Q$.

5-sulfonic acid ($LH_2^\pm$) at the same condition are 3.75 and 8.26 respectively). The equilibrium constants ($Q$) for the following processes,

$$Fe^{3+} + LH_2^+ \leftrightarrows FeL^{2+} + 2\,H^+, \qquad (i)$$

($LH_2^+$ represents the protonated form of oxine)

and

$$Fe^{3+} + LH_2^\pm \leftrightarrows FeL^+ + 2\,H^+ \qquad (ii)$$

($LH_2^\pm$ represents the protonated form of 8-hydroxyquinoline-5-sulfonate) were determined spectrophotometrically by varying $T_{Fe}$ (0.0025—0.008 mol dm$^{-3}$) at $T_L=0.00025$ mol dm$^{-3}$ and $[H^+]=0.15$ mol dm$^{-3}$.

$$T_{Fe} = [Fe^{3+}] + [Fe(OH)^{2+}] + [FeL^{2+/1+}] \approx [Fe^{3+}],$$

when $T_{Fe} \gg T_L$.

Under this condition, i.e. $[H^+] \gg T_{Fe} \gg T_L$ the above process leads to

$$\frac{1}{A-A_0} = \frac{[H^+]^2}{T_{Fe}} \times \frac{1}{QT_L\varepsilon l} + \frac{1}{T_L\varepsilon l}, \qquad (1)$$

where $A$=absorbance of the solution at equilibrium at $\lambda_{max}$ of $FeL^{2+/1+}$, $A_0$=absorbance of the corresponding iron solution at the same wavelength in absence of the ligand, $\varepsilon$=molar extinction coefficient of $FeL^{2+/1+}$ at $\lambda_{max}$, $l$=path length of the cell. Hence, the values of equilibrium constants, $Q$ could be evaluated by the least squares method ($Q$=intercept/slope) from a linear plot (cf. Fig. 1) of $1/(A-A_0)$ versus $[H^+]^2/T_{Fe}$. From the $Q$ values obtained at different temperatures, the corresponding $\Delta H$ and $\Delta S$ values could be evaluated (Table 1) graphically. The equilibrium constants obtained from spectrophotometric studies have been compared (Table 1) with those obtained from kinetic studies, and reported formation constants ($\beta_1$) of the complexes and the p$K_a$ values of the ligands.

**(b) Kinetics of Complex Formation:** Under the experimental conditions, ($T_{Fe}$=0.003—0.009 mol dm$^{-3}$, $T_L$=0.0003—0.0005 mol dm$^{-3}$; $[HClO_4]$=0.045—0.10 mol dm$^{-3}$; at $I$=1.0 mol dm$^{-3}$ ($NaClO_4$+$HClO_4$)) at the $\lambda_{max}$ of the corresponding complex, on the oscilloscope of stopped flow system, rising of absorbance with time indicates the attainment of the equilibria (i) and (ii) from left hand side i.e., formation of the complex. The mechanism consistent with the experimental observations (when $T_{Fe}/T_L \geqslant 10$) is as follows:

$$\begin{array}{l} Fe^{3+}_{aq} + LH_2^{+/\pm} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeL_{aq}^{2+/1+} + 2H^+, \quad Q=k_1/k_{-1} \\ K_h(-H^+)\Big\downarrow\!\Big\uparrow \\ Fe(OH)^{2+}_{aq} + LH_2^{+/\pm} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeL_{aq}^{2+/1+} + H^+, \quad Q/K_h = \dfrac{k_2}{k_{-2}} \end{array}$$

Scheme 1.

($LH_2^+$ and $LH_2^\pm$ stand for protonated 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonate respectively).

Such a dual path mechanism in which both $Fe^{3+}_{aq}$ $Fe(OH)^{2+}_{aq}$ react with the protonated or undissoociated ligand and where the proton transfer step is rapid have been found previously[15,16,22–24]. The above scheme leads[17] to tho following rate equation (when $[H^+] \gg T_{Fe} \gg T_L$),

$$k_{obsd} = T_{Fe}\frac{(k_1[H^+]+k_2K_h)}{K_h+[H^+]} + \frac{[H^+]}{Q}(k_1[H^+]+k_2K_h), \qquad (2)$$

or,

$$k_{obsd}/B = k_1[H^+] + k_2K_h, \qquad (3)$$

where $B = \dfrac{T_{Fe}}{[H^+]+K_h} + \dfrac{[H^+]}{Q}$.

At a fixed $[H^+]$, according to the Eq. 2, $k_{obsd}$ versus $T_{Fe}$ gives a linear plot with positive slope and intercept from which $Q$ could be evaluated as follows,

$$Q = [H^+]([H^+]+K_h) \times \frac{\text{slope}}{\text{intercept}}.$$

Thus $Q$'s obtained are compared (Table 1) with those obtained from spectrophotometric method and found in good agreement within the experimental error limit.

Here it is important to mention that the evaluated $Q$ values (average values of spectrophotometric and kinetic data) are also in fairly good agreement with those calculated (Table 1) from the reported [21] formation constants ($\beta_1$) of the mono-complex, $FeL^{2+/1+}$ and p$K_a$ values of the ligands. $Q$ can be expressed as,

$$Q = \beta_1 K_{a(1)} \times K_{a(2)}$$

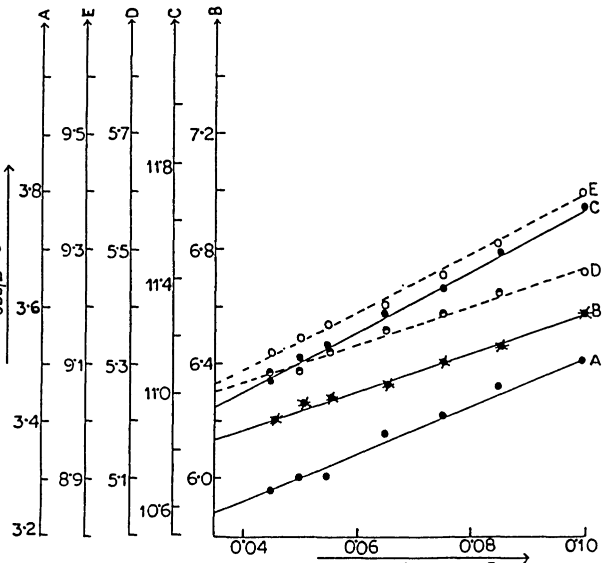

Fig. 2. Evaluation of $k_1$ and $k_2$ from the attainment of the equilibrium at lower acidities leading to the formation of the complex (cf. Eq. 3)

$$B = \frac{T_{Fe}}{[H^+]+K_h} + \frac{[H^+]}{Q}$$

$T_{Fe}$=0.003—0.009 mol dm$^{-3}$, $T_L$=0.0003—0.0005 mol dm$^{-3}$, $[HClO_4]$=0.045—0.1 mol dm$^{-3}$; $I$=1.0 mol dm$^{-3}$ ($NaClO_4$+$HClO_4$) (in the experimental set, $T_{Fe}/T_L \geqslant 10$). A(35 °C), B(40 °C), C(45 °C) for 8-hydroxyquinoline-5-sulfonate; D(40 °C), E(45 °C) for 8-hydroxyquinoline.

Table 2. Kinetic Parameters of Interaction of Iron(III) with 8-Hydroxyquinoline and 8-Hydroxyquinoline-5-sulfonic Acid in Acid Media

| System | Temp/°C | $k_1$ | $k_{-1}$ | $10^{-3}k_2$ | $k_{-2}$ |
|---|---|---|---|---|---|
| | | $dm^3\,mol^{-1}\,s^{-1}$ | $dm^6\,mol^{-2}\,s^{-1}$ | $dm^3\,mol^{-1}\,s^{-1}$ | $dm^3\,mol^{-1}\,s^{-1}$ |
| Iron(III)-8-hydroxyquinoline | | | | | |
| | 35 | 2.16±0.06 | 19.63±0.10 | 0.90±0.04 | 24.13±0.20 |
| | | (2.04±0.04) | (18.54±0.15) | (0.96±0.04) | (25.74±0.40) |
| | 40 | 3.18±0.09 | 21.93±0.20 | 1.34±0.05 | 35.48±0.40 |
| | | (3.08±0.08) | (21.24±0.10) | (1.30±0.03) | (34.43±0.40) |
| | 45 | 4.70±0.10 | 24.73±0.20 | 1.82±0.08 | 46.93±0.60 |
| | | (4.50±0.10) | (23.68±0.30) | (1.90±0.04) | (49.00±0.70) |
| $\Delta H^{\ne}$ | ($kJ\,mol^{-1}$) | 62±3 | 17±1 | 54±2 | 50±3 |
| $\Delta S^{\ne}$ | ($J\,K^{-1}\,mol^{-1}$) | −40±4 | −167±6 | −13±1 | −57±4 |
| Iron(III)-8-hydroxyquinoline-5-sulfonic acid | | | | | |
| | 35 | 4.24±0.10 | 23.55±0.20 | 1.05±0.02 | 17.20±0.20 |
| | | (4.32±0.04) | (24.00±0.20) | (1.01±0.01) | (16.55±0.08) |
| | 40 | 6.62±0.08 | 28.17±0.20 | 1.54±0.03 | 25.16±0.20 |
| | | (6.58±0.08) | (28.00±0.40) | (1.46±0.02) | (23.85±0.40) |
| | 45 | 9.95±0.10 | 32.41±0.40 | 2.17±0.04 | 34.63±0.60 |
| | | (10.05±0.06) | (32.73±0.60) | (2.13±0.04) | (34.00±0.40) |
| $\Delta H^{\ne}$ | ($kJ\,mol^{-1}$) | 67±3 | 23±1 | 58±2 | 56±3 |
| $\Delta S^{\ne}$ | ($J\,K^{-1}\,mol^{-1}$) | −17±1 | −145±8 | −1±0 | −42±2 |

Rate constants in parentheses are obtained from the dissociation study while the others are obtained from formation study. Activation parameters are calculated by using averages of these values.

Formation study: $T_{Fe}$, 0.003—0.009 mol dm$^{-3}$; $T_L$, 0.0003—0.0005 mol dm$^{-3}$; and $T_{Fe}/T_L \geqslant 10$; [H$^+$], 0.045—0.10 mol dm$^{-3}$.

Dissociation study: $T_{Fe}$, 0.003 mol dm$^{-3}$; $T_L$, 0.00025 mol dm$^{-3}$; [H$^+$], 0.50—1.0 mol dm$^{-3}$; $I$=1.0 mol dm$^{-3}$ (NaClO$_4$+HClO$_4$); $\lambda$=645 nm and 625 nm for 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid respectively.

where, $LH_2 \overset{K_{a(1)}}{\rightleftarrows} LH+H^+$; $LH \overset{K_{a(2)}}{\rightleftarrows} L+H^+$; and $M+L \overset{\beta_1}{\rightleftarrows} ML$, charges are omitted for simplicity.

$k_{obsd}/B$ versus [H$^+$] gives a straight line (cf. Eq. 3 and Fig. 2) with positive slopes and intercepts (evaluated by the least squares method) from which $k_1$ and $k_2$ could be evaluated. By using these values along with those of Q, $k_{-1}$ and $k_{-2}$ could be evaluated (Table 2).

**Kinetics of Acid Catalysed Dissociation of the Mono-Complex:** The mono-ccomplex was prepared at low acid concentration ($T_{Fe}$, 0.006 mol dm$^{-3}$; $T_L$, 0.00050 mol dm$^{-3}$; [H$^+$], 0.045 mol dm$^{-3}$; $I$=1.0 mol dm$^{-3}$). Thus the prepared complex remaining at an equilibrium taken in one of the syringes of the stopped flow system was treated with an excess acid along with the requisite amount of NaClO$_4$ (taken in the other syringe of the stopped flow sytem) so that [H$^+$] becomes 0.5—1.0 mol dm$^{-3}$ and $I$=1.0 mol dm$^{-3}$ during the reaction in the stopped-flow spectrophotometer. At that condition, the oscilloscope trace showed at $\lambda_{max}$ of the complex the decay of absorbance with time. This suggests the attainment of the equilibria (i) and (ii) from right hand side to the left hand side i.e., dissociation of the complex. In this case, assuming the principle of reversibility to be true, the Scheme 1 leads to the following rate equation.

$$k_{obsd}/C = k_{-1}[H^+] + k_{-2}, \qquad (4)$$

where
$$C=[H^+]+\frac{QT_{Fe}}{[H^+]+K_h}.$$

The experimental observations nicely fit (cf. Fig. 3) into this equation and the different rate constants, $k_1$, $k_2$, $k_{-1}$, and $k_{-2}$ (Table 2) obtained in this way agree well with those obtained from formation study.

In the both systems, $k_1$ path is unfavored with respect to $k_{-1}$ path due to higher $\Delta H^{\ne}$ values in the forward path. Though the $\Delta H^{\ne}$ values for $k_{-1}$ paths are smaller but due to high negative values of $\Delta S^{\ne}$, these are unfavored. In both the systems, $\Delta H$ for $Q$=($k_1/k_{-1}$) is positive and the process is favored by the entropy factor.

According to Eigen mechanism,[2] the magnitude of overall rate constant ($k=k_{ex}K_{os}$) depends upon both the outer-sphere association constant ($K_{os}$) and the first order rate constant of water exchange ($k_{ex}$). $K_{os}$ can be computed roughly as 0.04 mol$^{-1}$ dm$^3$ in the case of 8-hydroxyquinoline ($Z_AZ_B$=2) in $k_2$ path with the help of Fuoss Equation.[25] In the case of sulfonate derivative, the additional 1- charge imparted by -SO$_3^-$ group is expected not to enhance the electrostatic attraction. Hence, it is reasonable to consider the magnitude of $K_{os}$ 0.04 mol$^{-1}$ dm$^3$ as in the case of 8-hydroxyquinoline. From the $k_2$ values which are evaluated without any proton ambiguity, $k_{ex}$ becomes 1.10×10$^4$ s$^{-1}$ (=443.0/0.04) and 1.12×10$^4$ s$^{-1}$ (=449.4/0.04) at 25 °C for 8-

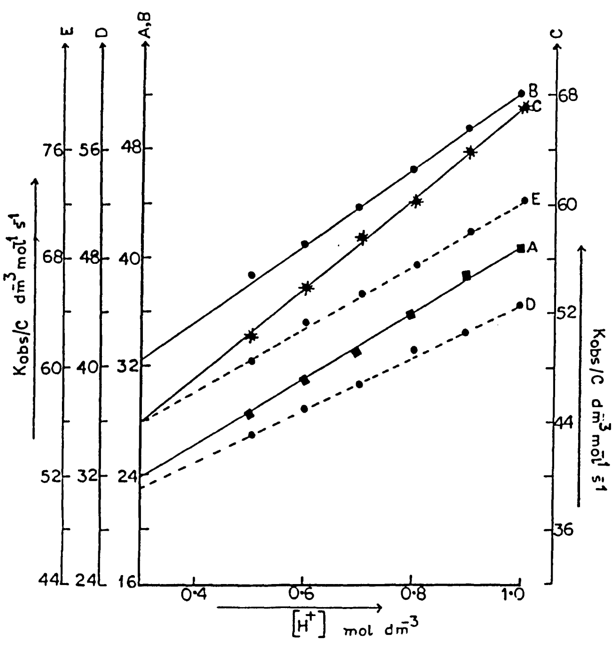

Fig. 3. Evaluation of $k_{-1}$ and $k_{-2}$ form the attainment of the equilibrium at higher acidities leading to the dissociation of the complex (cf. Eq. 4)

$$C=[\mathrm{H}^+]+\frac{T_{\mathrm{Fe}}Q}{K_{\mathrm{h}}+[\mathrm{H}^+]}$$

$T_{\mathrm{Fe}}=0.003$ mol dm$^{-3}$, $T_{\mathrm{L}}=0.00025$ mol dm$^{-3}$, $[\mathrm{H}^+]=0.50$—1.00 mol dm$^{-3}$. $I=1.0$ mol dm$^{-3}$ ($NaClO_4$+$HClO_4$). A(35 °C), B(40 °C), C(45 °C) for Fe(III)-8-hydroxyquinoline-5-sulfonate; D(35 °C), E(45 °C) for Fe(III)-8-hydroxyquinoline.

hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid systems respectively. The closeness of these values of $k_{\mathrm{ex}}$ with those obtained[8)] in the range $(0.1—8.0)\times 10^4\ \mathrm{s}^{-1}$ at 25 °C for a series of ligands of quite different structure, binding sites and basicity indicates the dissociative mechanism of $\mathrm{Fe(OH)}_{\mathrm{aq}}^{2+}$ and it can be regarded as a normal divalent cation[1,2,4,26)]. Such a dissociative behavior has been established without any proton ambiguity in the series of chloro-, dichloro-, and trichloroacetic acids.[27)]

If the same type of dissociative mechanism is supposed to be operative for the $k_1$ path also (where $K_{\mathrm{os}}$ can be roughly computed as 0.015 mol$^{-1}$ dm$^3$ for $Z_{\mathrm{A}}Z_{\mathrm{B}}=3$ by using the Fuoss Equation),[25)] then the water exchange rate ($k_{\mathrm{ex}}$) for $\mathrm{Fe}_{\mathrm{aq}}^{3+}$ becomes 66.6 s$^{-1}$ (=1.0/0.015) and 128 s$^{-1}$ (=1.92/0.015) at 25 °C for 8-hydroxyquinoline and its sulfonate derivative respectively. In fact, thus the calculated $k_{\mathrm{ex}}$ values ($=k_1/K_{\mathrm{os}}$) are found to vary[19)] in a wide range 9.0 to $9.5\times10^5\ \mathrm{s}^{-1}$ depending on the nature of the entering ligand. Thus in the case of $\mathrm{Fe}_{\mathrm{aq}}^{3+}$ the variation of rate constant ($k_1$) cannot be explained due to the variation of $K_{\mathrm{os}}$, rather it is markedly dependent on the nature, structure and basicity of the ligands and it suggests some associative character in the case of ligand substitution process. Such $I_{\mathrm{a}}$ mechanism is also found in the cases of Mo(III).[28)] In the present investigations, the slower rates in the case of $k_1$ path (=0.99 dm$^3$ mol$^{-1}$ s$^{-1}$ and 1.92 dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C for 8-hydroxyquinoline and its sulfonic acid derivative respectively) with respect to phenol[12)] ($k_1$=25 dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C) suggests the sluggishness due to the ring closure step. Here the most striking aspect is that the dissociative mechanism argued for $\mathrm{Fe(OH)}_{\mathrm{aq}}^{2+}$ does not have, however, any implication on the character of $\mathrm{Fe}_{\mathrm{aq}}^{3+}$ from the kinetic point of view, though they are inter-related by a protolytic equilibrium.

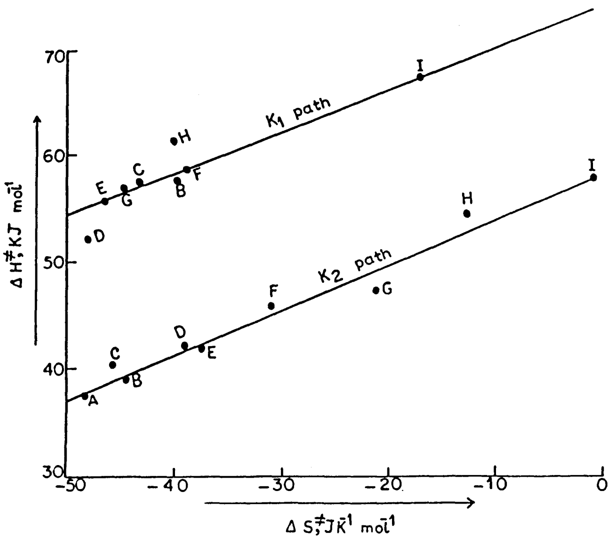

Fig. 4. $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ plots (isokinetic trend). A=salicylhydroxamic acid, B=benzohydroxamic acid, C=*ortho*-chlorobenzohydroxamic acid, D=salicylaldehyde, E=*ortho*-methylbenzohydroxamic acid, F=*ortho*-hydroxyacetophenone, G=*ortho*-aminobenzohydroxamic acid, H=8-hydroxyquinoline, I=8-hydroxyquinoline-5-sulfonic acid. (for hydroxamic acids Ref. 15, for D and F Ref. 16).

The activation parameters (i.e, $\Delta H^{\neq}$, $\Delta S^{\neq}$) determined are in fact composite ones[19)] involving the $\Delta H$ and $\Delta S$ values of outersphere association constants, deprotonation processes of the involved ligand, etc. A fairly good linear plot, $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ (cf. Fig. 4) for both $k_1$ and $k_2$ paths for different hydroxamic acids,[15)] phenols[16)] along with the present ligands indicates a similarity of mechanism for each path for all the ligands.

Very recently, the equilibria and dynamics of interaction of Ce(IV) with the present studied ligands in perchloric acid media have been reported.[17)] Thus the present results provide a worthy comparison. Fe(III) and Ce(IV) are the members of ‘d’ and ‘f’ block elements respectively but the same type of dual path mechanism involving $\mathrm{M}^{n+}$ and $\mathrm{M(OH)}^{(n-1)+}$ is operative[17)] in the metal centers. For both the metal centers i.e., Fe(III) and Ce(IV), the $k_1$ path is sensitive (i.e., $\mathrm{I_a}$ process) to the ligands while the $k_2$ path is insensitive (i.e., $\mathrm{I_d}$ process) to the entering ligands. One striking difference between the two metal centers is that after the formation of the complex in the case of Ce(IV), there occurs an intramolecular electron transfer from ligand moiety to metal center and it undergoes a redox decomposition relatively slowly. On the other hand, Fe(III) forms a very stable complex where no such redox reaction occurs. For 8-hydroxyquinoline and its sulfonic acid derivative the values[17] of $Q$ for Ce(IV) are ca. $7.1\times10^3$ and ca. $10.2\times10^3$ times greater than the corresponding values for Fe(III) at 35 °C. This suggests Ce(IV) to form thermodynamically more stable complexes and it is due to lower $\Delta H$ values (ca. 14—15 kJ mol$^{-1}$ while for Fe(III) it is ca. 44 kJ mol$^{-1}$) for Ce(IV) systems as $\Delta S$ values (ca. 101—112 J K$^{-1}$ mol$^{-1}$ while for Fe(III) it is 127 J K$^{-1}$ mol$^{-1}$) are more or less same for both the metal ions. In terms of kinetic parameter, the higher values of $Q$ for Ce(IV) systems arise due to the higher values of $k_1$ (by about $10^3$) as $k_{-1}$ values are more or less constant for both the metal centers. $k_1$ paths for Ce(IV) systems are favored mainly due to lower $\Delta H^{\neq}$ (ca. 29 kJ mol$^{-1}$ while for Fe(III) it is ca. 62—67 kJ mol$^{-1}$) values. Here it is worth noting that for Fe(III) systems, $k_2$ path i.e., monohydroxo species is ca. $10^3$ times more reactive than $k_1$ path i.e., $Fe_{aq}^{3+}$ species while for Ce(IV) system, no such marked enhanced reactivity for $k_2$ path is noticed and both the paths are almost equally active.

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