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Kinetics of the Complexation of Ferric Iron with 8-Hydroxyquinoline and Kelex-100

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ABSTRACT

The complexation reactions of ferric iron with 8-Hydroxyquinoline and KELEX-100 in both aqueous and methanol solutions were studied by using a stopped-flow spectrophotometer. In the aqueous solutions, the observed rate law was found to be first-order with respect to both iron(III) and oxine and inverse-first-order with respect to the hydrogen ion. While in the methanol solution, the rate law was first-order with respect to iron(III) and KELEX-100. Reaction pathes with the formation of the first complex, FeA^{2+}, from either Fe^{3+} or $Fe(OH)^{2+}$ were proposed to explain the observed rate law. The activation energies were found to be 5.5 kcal/g-mole and 15 kcal/g-mole for the aqueous and methanol solutions, respectively.

INTRODUCTION

There are some interesting studies of the complexation reaction of iron(III) with KELEX-100 (1, 2, 3) and its base reagent, oxine (4, 5, 6, 7). Most of the former studies were carried out in a heterogeneous system in which both diffusion and chemical reaction occur simultaneously. Although solvent extraction is a heterogeneous process, homogeneous studies of the chemical reactions involved should always be considered. These homogeneous studies provide knowledge of the intrinsic kinetics of the chemical reactions involved in the extraction. This information allows for a more complete evaluation of the data obtained from a heterogeneous study.

In this investigation, the reactions are carried out using a stopped-flow spectrophotometer to eliminate the diffusion process.

Methanol was the solvent for KELEX-100 which is negligibly soluble in water, but both water and methanol are used for the oxine reaction system.

EXPERIMENTAL

All the reagents used here are ACS grade chemicals except KELEX-100 which is obtained from Sherex Chemical Company, Dublin, Ohio. The commercial KELEX-100 is purified by dissolving in toluene, extracted by acidic aqueous solution, washing with distilled water and then a vacuum evaporation (8). Ionic strengths were adjusted by addition of sodium perchlorate. Acidity of the reaction solution was adjusted by adding concentrated hydrochloric acid. In all cases iron(III) was in excess.

Reactions were studied by a Durrum-Gibson Model D-110 stopped-flow spectrophotometer at the wavelength of 600 nm., which was corresponding to a maximum absorbance of the complex. Temperature of the reaction solution was kept within ±0.1°C. Reaction curves were recorded by a strip chart recorder.

DATA ANALYSIS

Since the formation of mono-complex, FeA^{2+}, is favored according to studies of the equilibrium (9, 10-13), the complexation reaction can be expressed as

$$Fe^{3+} + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeA^{2+} + H^+ \qquad (1)$$

In spite of the complex reaction mechanism, the experimental rate equation can be written in a power-law form as

$$\frac{d[FeA^{2+}]}{dt} = k_1[Fe^{3+}]^a[HA]^b - k_{-1}[FeA^{2+}]^c[H^+]^d \qquad (2)$$

If $[Fe^{3+}]$ and $[H^+]$ are kept as constants during the reaction and the reaction order b and c are assumed as first-order, the above rate equation can be simplified to

$$\frac{d[FeA^{2+}]}{dt} = k_{obs}([FeA^{2+}]_\infty - [FeA^{2+}]) \qquad (3)$$

which can be integrated to obtain

$$\ln\left\{\frac{[\mathrm{FeA}^{2+}]_\infty - [\mathrm{FeA}^{2+}]}{[\mathrm{FeA}^{2+}]_\infty - [\mathrm{FeA}^{2+}]_0}\right\} = k_{obs}\, t \qquad (4)$$

where $k_{obs} = k_1[\mathrm{Fe}^{3+}]^a + k_{-1}[\mathrm{H}^+]^d$, (5)

and, $[\mathrm{FeA}^{2+}]_0$ and $[\mathrm{FeA}^{2+}]_\infty$ represent initial and equilibrium concentration, respectively.

The above integrated rate equation may be converted into optical absorbance form (14) if the Beer's law is followed and the addition of absorbances prevails. The final form is

$$\ln\left\{\frac{A_t - A_\infty}{A_0 - A_\infty}\right\} = k_{obs}\, t \qquad (6)$$

RESULTS

Observed rate equation and rate constant. The reaction curves may be presented by plotting $\ln[(A_t - A_\infty)/(A_o - A_\infty)]$ versus reaction time as shown in Figures 1 through 3. The straight lines indicate that the first-order reaction with respect to the ligand is a reasonable assumption.

The observed rate constants, k_{obs}, can then be calculated from the slopes of the straight lines and are shown (with their standard deviation) in Tables 1 through 4.

The values of k_{obs} can be plotted against the concentration of iron(III) as shown in Figures 4 through 6. A good straight line indicates that the reaction order with respect to iron(III) is also first-order. The best fitted equations for k_{obs} may be expressed as,

$$k_{obs} = 0.05 + (90.15 + 0.0734\ \mathrm{H}^{+\ -1})\ \mathrm{Fe}^{3+} \quad \mathrm{sec}^{-1} \qquad (7)$$

for the iron(III)-oxine reaction in aqueous solution,

$$k_{obs} = (717.7)\ \mathrm{Fe}^{3+} \quad \mathrm{sec}^{-} \qquad (8)$$

for the iron(III)-oxine reaction in methanol solution,

$$k_{obs} = (360.8)\ \mathrm{Fe}^{3+} + 0.026 \quad \mathrm{sec}^{-1} \qquad (9)$$

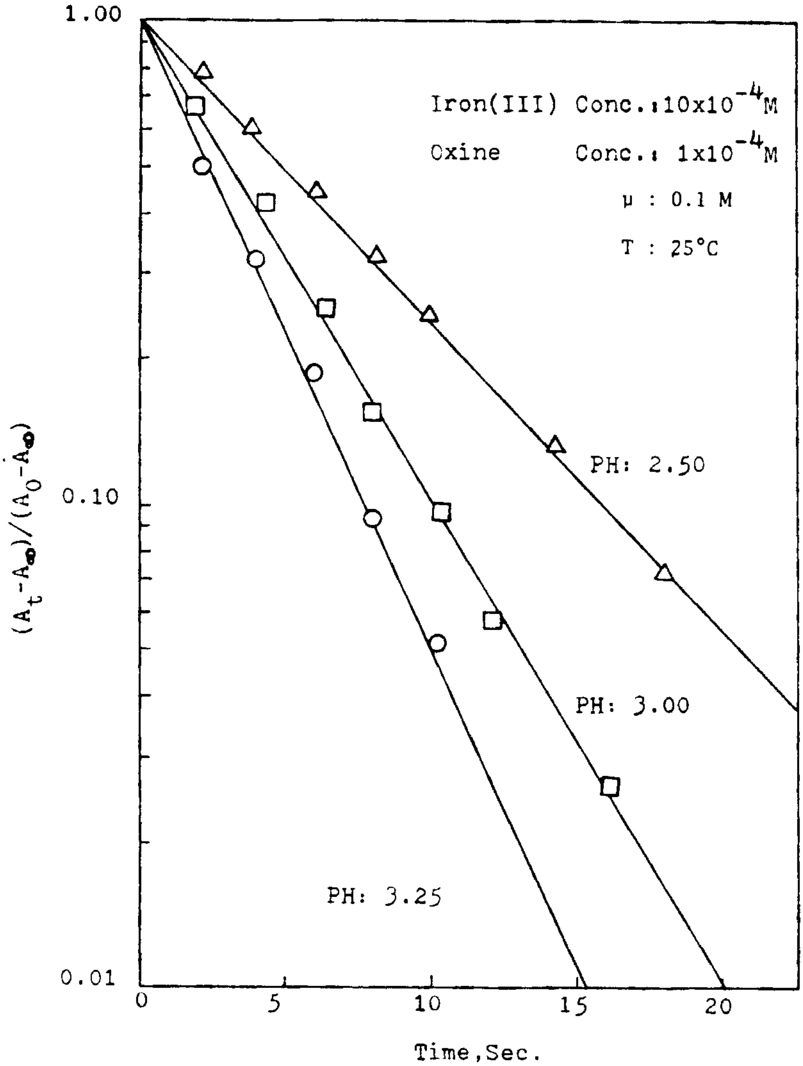

Figure 1. Iron(III)-oxine Reaction Curves in Aqueous Solution.

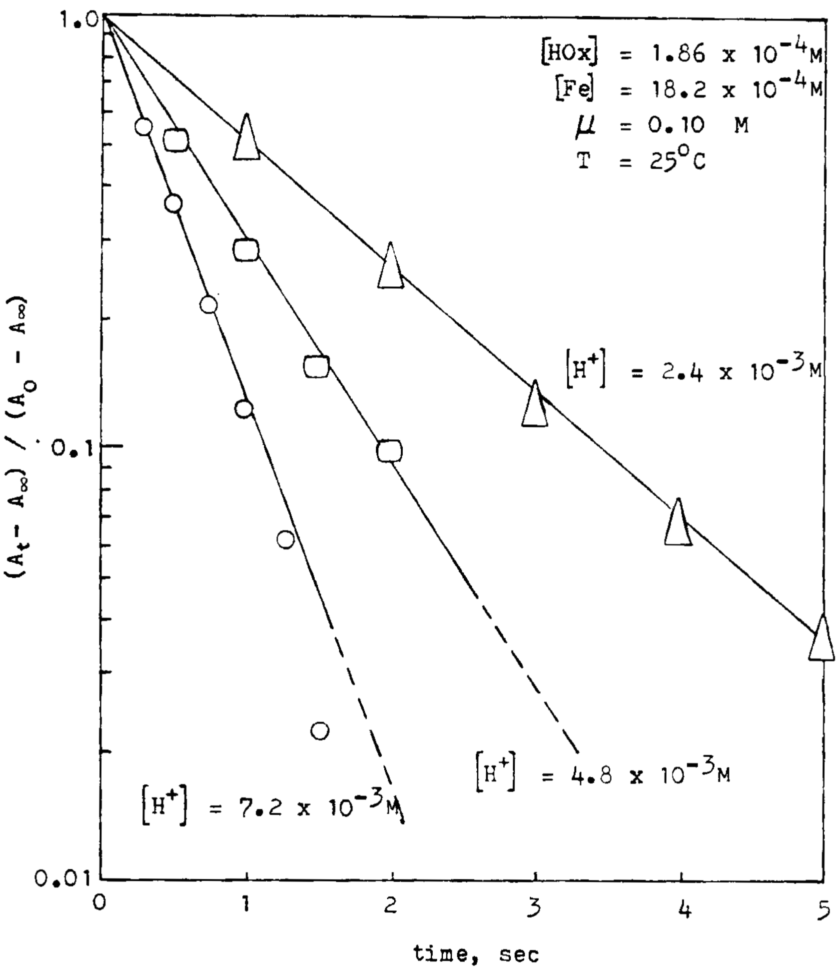

Figure 2. Typical reaction curves for the reaction of ferric iron with oxine in methanol solution.

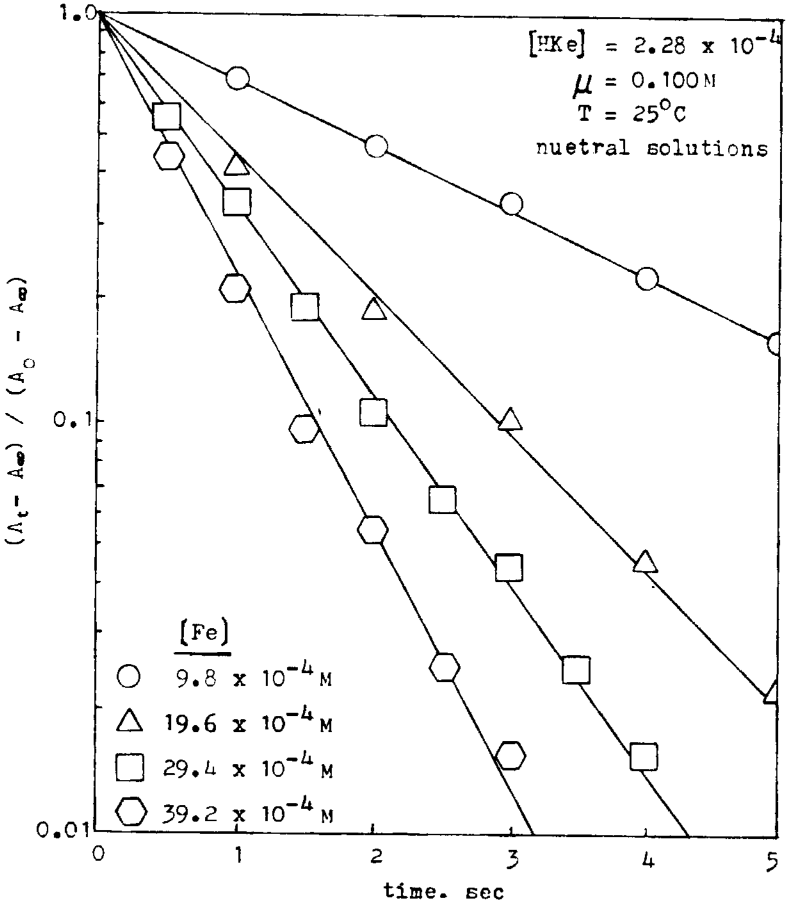

Figure 3. Typical reaction curves for the reaction of ferric iron with KELEX-100 in methanol solution.

TABLE 1.

Reaction Rate Constants[a] of Iron(III)-Oxine Complexation Reaction at 25.0±0.1 °C

pH	[Fe(III)] $\times 10^4$,M	k_{obsd},sec^{-1}	S.D.(σ),sec^{-1}
2.50	2	0.0691	0.0038
2.50	4	0.0844	0.0021
2.50	5	0.0986	0.0036
2.50	8	0.1263	0.0155
2.50	10	0.1415	0.0069
2.50	15	0.1925	0.0270
2.50	20	0.2662	0.0397
2.75	2	0.0771	0.0113
2.75	4	0.1020	0.0142
2.75	5	0.1155	0.0184
2.75	8	0.1566	0.0282
2.75	10	0.1883	0.0035
2.75	15	0.2691	0.0668
2.75	20	0.3211	0.0741
3.00	2	0.0928	0.0086
3.00	4	0.1271	0.0198
3.00	5	0.1603	0.0098
3.00	8	0.1670	0.0340
3.00	10	0.2430	0.0282
3.00	15	0.2977	0.0335
3.00	20	0.4090	0.0260
3.25	2	0.1079	0.0084
3.25	4	0.1440	0.0250
3.25	5	0.1684	0.0126
3.25	8	0.1916[b]	0.0154
3.25	10	0.2720[b]	------

a) $[\mathrm{Oxine}]_o$ -1×10^{-4}M, k_{obsd} were obtained from the average value of three runs.

b) Value of k_{obsd} was obtained from one run

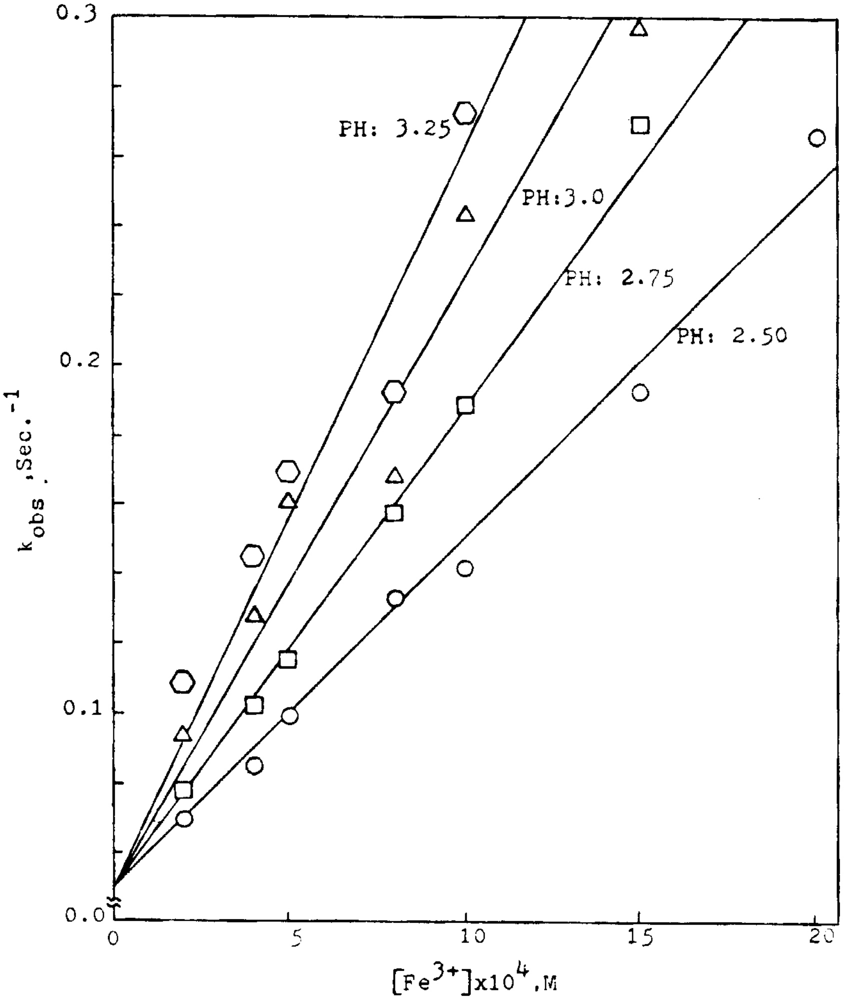

Figure 4. Plot of k_{obsd} Values versus Iron(III) at Different PH Values

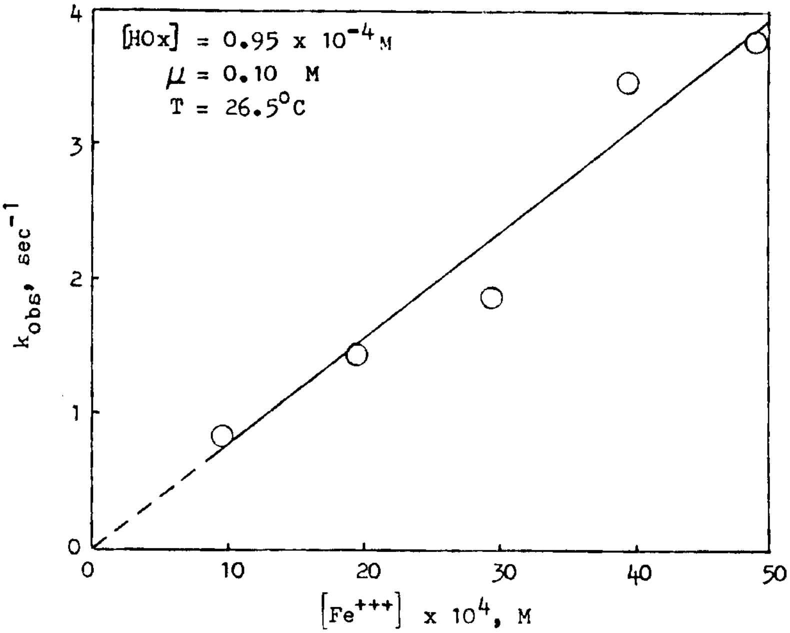

Figure 5. Variation of the rate constant with iron concentration for the reaction of oxine with ferric iron in methanol.

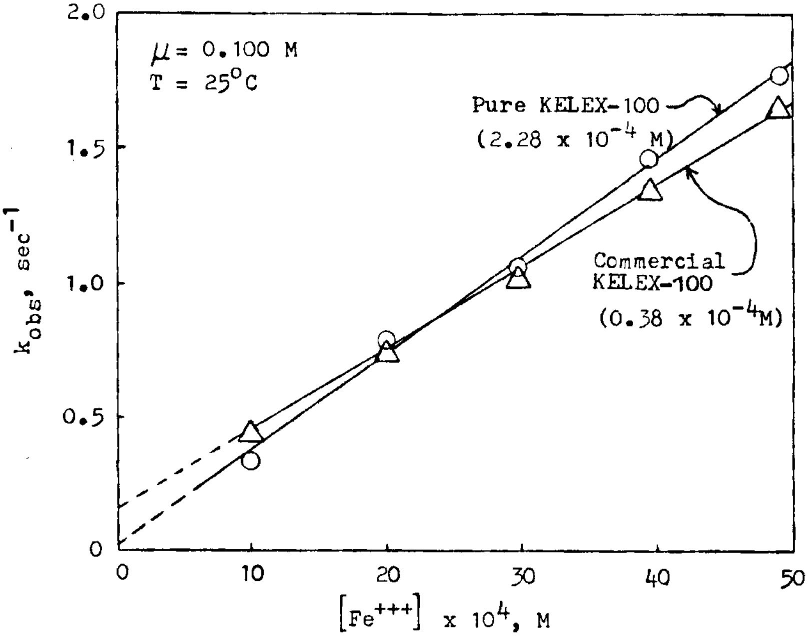

Figure 6. Variation of the rate constant with iron concentration for the reaction of KELEX-100 with ferric iron in methanol.

TABLE 2.

Observed rate constants for the oxine-ferric iron complexation reaction in methanol.

[HOx] (x 10^4M)	[Fe^{+++}] (x 10^4M)	μ (M)	Temp. (^oC)	k_{obs}^{a} (sec^{-1})	σ (sec^{-1})
0.95	9.8	0.100	26.4	0.8157^b	0.0139
0.95	19.6	0.100	26.4	1.4306^b	0.0660
0.95	29.4	0.100	26.6	1.8442^b	0.0639
0.95	39.2	0.100	26.9	3.4635^b	0.1835
0.95	49.0	0.100	26.9	3.7901^b	0.4702
0.96	10.1	0.100	14.3	0.2507^b	0.0078
0.96	10.1	0.100	24.9	0.6532	0.0198
0.96	10.1	0.100	34.8	1.2028	0.0455
0.96	10.1	0.100	44.6	2.8822	0.1957
1.81	19.4	0.202	25.6	1.4521^b	0.0631
1.81	19.4	0.401	26.5	1.5404^b	0.0600
1.81	19.4	0.604	26.6	1.6835^b	0.1006
1.81	19.4	0.803	26.6	1.9266^b	0.0136

a) Average of three kinetic runs.
b) Average of two kinetic runs

for the iron(III)-purified KELEX-100 reaction in methanol, and

$$k_{obs} = (340.9)\ Fe^{3+} + 0.142 \qquad sec^{-1} \qquad (10)$$

for iron(III)-commercial KELEX-100 reaction in methanol.

Temperature Effect. Results of the effect of temperature on the rate constant, k_{obs}, are shown on Figures 7 and 8. The activation energies obtained from the Arrhenius plot are 5.5 Kcal/gmole for iron(III)-oxine reaction in aqueous solution, 14.3 Kcal/gmole for iron(III)-oxine reaction in methanol solution, and 15.3 Kcal/gmole for iron(III)-KELEX-100 reaction in methanol solution.

Ionic Strength Effect. The effect of ionic strength on the observed rate constant has been studied for the reaction in methanol solution and is presented in Figures 9 and 10. It may be seen that the rate constant of iron(III)-oxine reaction increases while that of iron(III)-KELE-100 decreases as the ionic strength increases.

TABLE 3

Observed rate constants for the KELEX-100-ferric iron complexation reaction using pure KELEX-100 in methanol.

[HKe] (x 10^4M)	[Fe^{+++}] (x 10^4M)	μ (M)	Temp. (^oC)	k_{obs}[a] (sec^{-1})	σ (sec^{-1})
2.28	9.8	0.100	24.4	0.3356	0.0138
2.28	19.6	0.100	24.6	0.7942	0.0246
2.28	29.4	0.100	25.0	1.0696	0.0552
2.28	39.2	0.100	25.2	1.4663	0.0263
2.28	49.0	0.100	25.2	1.7677[b]	0.1102
2.28	9.8	0.100	24.4	0.3356	0.0138
2.28	9.8	0.100	35.0	0.5227	0.0414
2.28	9.8	0.100	40.3	0.9794	0.0443
2.28	9.8	0.100	44.9	1.7447[b]	0.1518
2.28	9.8	0.100	50.7	2.4431	0.0732
3.04	18.8	0.200	24.3	0.4457	0.0038
3.04	18.8	0.397	24.6	0.4212	0.0123
3.04	18.8	0.600	25.0	0.3923	0.0255
3.04	18.8	0.800	25.5	0.4532	0.0425
3.04	18.8	1.000	25.6	0.3496	0.0576

a) Average of three kinetic runs
b) Average of two kinetic runs

By using Perlmuter-Hayman (15) correlation equation, the best fitted equation is

$$\ln(k_{obs}) = 1.292\mu - 1.110\mu^{1/2} + 0.612 \qquad (11)$$

for iron(III)-oxine reaction in methanol solution,

$$\ln(k_{obs}) = -0.253\mu - 0.078\mu^{1/2} - 0.720 \qquad (12)$$

for iron(III)-KELEX-100 (purified) reaction in methanol solution, and

$$\ln(k_{obs}) = 0.699\mu - 1.416\mu^{1/2} + 0.0357 \qquad (13)$$

for iron(III)-KELEX-100 (commercial) reaction in methanol solution. Here is the ionic strength of the solution.

TABLE 4.

Observed rate constants for the KELEX-100-ferric iron complexation reaction using commercial KELEX-100 in methanol.

$[HKe]^c$ ($\times 10^4$M)	$[Fe^{+++}]$ ($\times 10^4$M)	μ (M)	Temp. (^oC)	$k_{obs}{}^a$ (sec^{-1})	σ (sec^{-1})
0.38	9.8	0.100	25.1	0.4315	0.0599
0.38	19.6	0.100	25.1	0.7737	0.0844
0.38	29.4	0.100	25.6	1.0110	0.0600
0.38	39.2	0.100	25.6	1.3270	0.0462
0.38	49.0	0.100	25.6	1.6490^b	0.0190
0.60	10.1	0.100	15.0	0.1514	0.0094
0.60	10.1	0.100	25.1	0.3278	0.0619
0.60	10.1	0.100	34.6	0.8120	0.1095
0.60	10.1	0.100	44.4	1.8555	0.1676
1.20	19.4	0.202	25.9	0.6395	0.0320
1.20	19.4	0.401	26.2	0.5444	0.0498
1.20	19.4	0.604	26.1	0.5237	0.0260
1.20	19.4	0.803	26.3	0.5235	0.0945
1.20	19.4	1.000	26.9	0.4965	0.0107

a) Average of three kinetic runs.
b) Average of two kinetic runs.
c) Concentration of commercial reagent expressed as 100% KELEX-100.

Reaction Pathes of the Complexation between Iron(III) and Oxine in Aqueous Solutions. In an aqueous solution the iron(III) may be hydrolyzed to monohydroxy iron, $Fe(OH)^{2+}$, as shown below,

$$Fe^{3+} + H_2O \rightleftarrows Fe(OH)^{2+} + H^+ \tag{14}$$

the hydrolysis equilibrium constant K_h is defined as:

$$K_h = \frac{[Fe(OH)^{2+}]\ [H^+]}{[Fe^{3+}]} \tag{15}$$

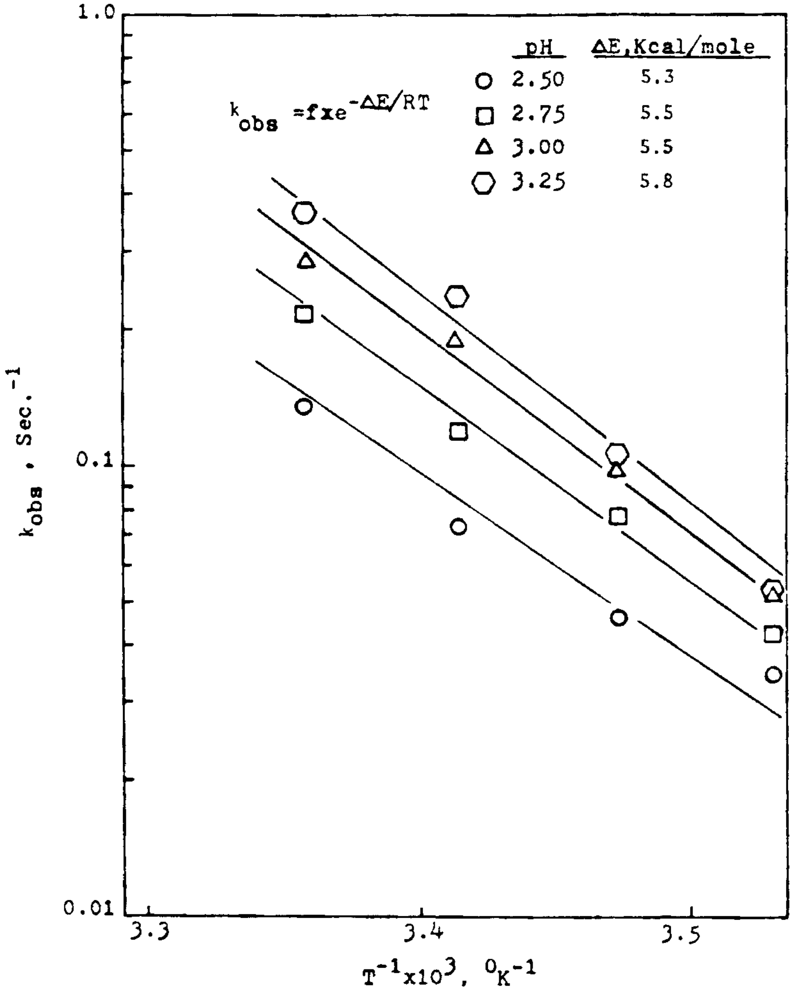

Figure 7. The effect of temperature on rate constant for iron (III)-oxine reaction in aqueous solution.

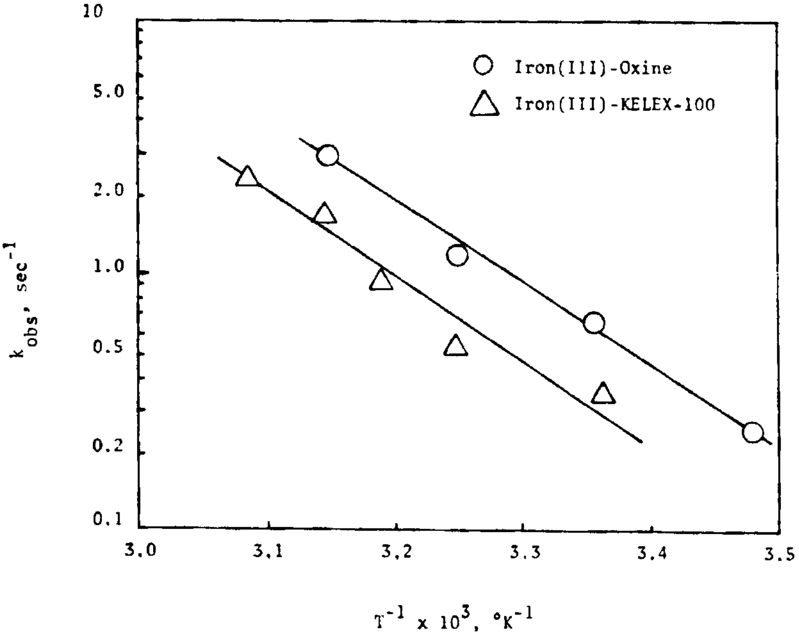

Figure 8. The effect of temperature on rate onstant in methanol solution.

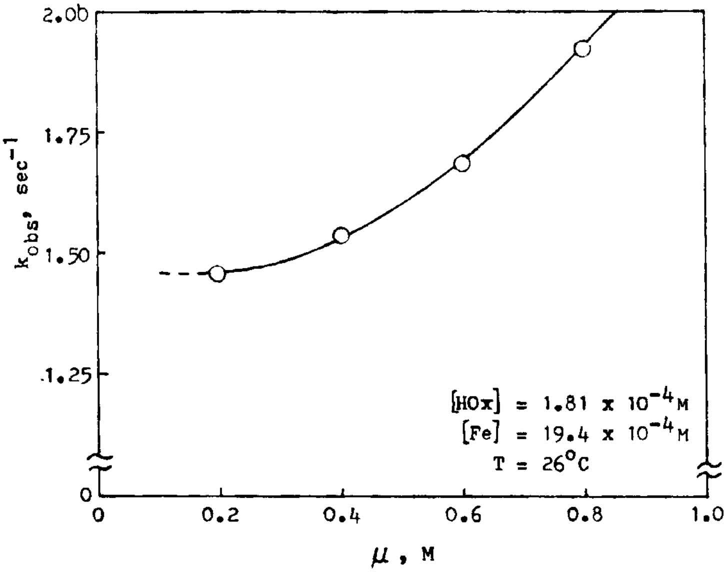

Figure 9. The effect of ionic strength on the rate constant for the reaction of oxine with ferric iron in methanol.

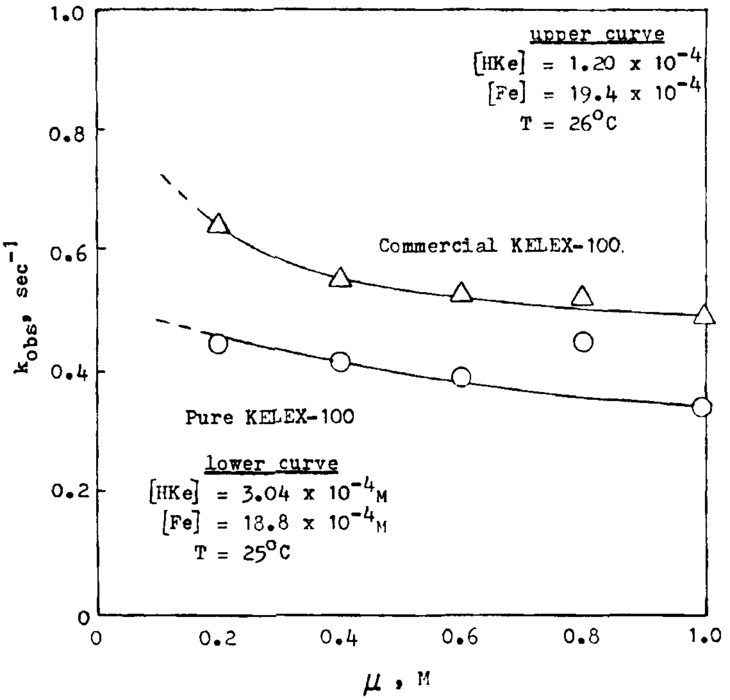

Figure 10. The effect of ionic strength on the rate constant for the reaction of KELEX-100 with ferric iron in methanol.

The value of K_h at 25°C and 1.0 M of $NaClO_4$ aqueous solution has been reported as 1.65 x 10^{-3}M (16). It has been reported that both the free metal ion iron(III) and the monohydroxy iron react readily with appropriate ligands to form a stable iron complex (17, 18, 19, 20, 21, 22).

Oxine is sparingly soluble in cold water (3.6 x 10^{-3}M at 20-25 °C), but readily soluble in mineral acids and in dilute alkalis to form yellow solutions. The increase of solubility in acid solutions is caused by the formation of hydroxyquinolium ions, H_2A^+, while in alkaline solutions oxinate ions, A^-, are formed (10). Therefore in the aqueous solution, HA, A^- and H_2A^+ are at equilibrium. The equilibrium equations are:

$$HA \rightleftarrows A^- + H^+ \qquad (16)$$

$$K_{HA} = \frac{[H^+][A^-]}{[HA]} = 10^{-9.66} \text{ (at 25 °C)}, \tag{17}$$

and $$H_2A^+ \rightleftarrows HA + H^+ \tag{18}$$

$$K_{H_2A^+} = \frac{[H^+][HA]}{[H_2A^+]} = 10^{-5.00} \text{ (at 25 °C)}. \tag{19}$$

During the reactions, it was assumed that both Fe^{3+} and $Fe(OH)^{2+}$ would react with HA and A^-, but not with H_2A^+ because both ion species are positively charged. Therefore, the possible reaction pathes for the complexation reaction between iron(III) and oxine in the aqueous solution are proposed as follows:

$$Fe^{3+} + HA \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} FeA^{2+} + H^+ \tag{20}$$

$$Fe(OH)^{2+} + HA \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} FeA^{2+} + H_2O \tag{21}$$

$$Fe^{3+} + A^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} FeA^{2+} \tag{22}$$

$$Fe(OH)^{2+} + A^- \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} FeA^{2+} + OH^- \tag{23}$$

The rate equation may be written as

$$\begin{aligned} \text{Rate} &= -\frac{d[HA]}{dt} = \frac{d[FeA^{2+}]}{dt} \\ &= k_1[Fe^{3+}][HA] - k_{-1}[FeA^{2+}][H^+] \\ &\quad + k_2[Fe(OH)^{2+}][HA] - k_{-2}[FeA^{2+}] \end{aligned}$$

$$+k_3[Fe^{3+}][A^-]-k_{-3}[FeA^{2+}]$$
$$+k_4[Fe(OH)^{2+}][A^-]-k_{-4}[FeA^{2+}][OH^-]. \qquad (24)$$

With the help of Equations (15) and (17) and the definition of K_w, $K_w = [H^+][OH^-]$, the above rate equation can be converted into

$$-\frac{d[HA]}{dt} = K_f[Fe^{3+}][HA]-K_r[FeA^{2+}] \quad , \qquad (25)$$

where $K_f = k_1+(k_2K_h+k_3K_{HA}+k_4K_h)[H^+]^{-1}$, (26)

and $K_r = k_{-1}[H^+]+k_{-2}+k_{-3}+k_{-4}K_w[H^+]$. (27)

Since iron(III) concentration is in large excess, i.e. $[Fe^{3+}]_o >> [HA]_o$ and FeA^{2+} is dominant among the products,

$$[HA]_0 = [HA]+[FeA^{2+}] \quad . \qquad (28)$$

Combine Equations (25) and (28) to obtain

$$\frac{d[FeA^{2+}]}{dt} = K_f[Fe^{3+}][HA]_0 - (K_f[Fe^{3+}] + K_r)[FeA^{2+}] \qquad (29)$$

As the reaction reaches equilibrium Equation (29) gives

$$K_f[Fe^{3+}]_\infty[HA]_0 = (K_f[Fe^{3+}]_\infty + K_r)[FeA^{2+}]_\infty \qquad (30)$$

Substitute Equation (30) into Equation (29) to obtain the rate equation as

$$\frac{d[FeA^{2+}]}{dt} = (K_f[Fe^{3+}]_\infty + K_r)([FeA^{2+}]_\infty - [FeA^{2+}]) \qquad (31)$$

As can be seen from Equations (31) and (3) that we have

$$k_{obs} = K_f[Fe^{3+}] + K_r \quad . \tag{32}$$

For iron(III)-oxine in aqueous solution, k_{obs} has been determined and can be seen in Equation (7). Therefore

$$K_f = 90.15 + 0.0734[H^+]^{-1} \qquad M^{-1}sec^{-1} \tag{33}$$

and

$$K_r = 0.05 \qquad Sec^{-1} \tag{34}$$

Equation (34) implies that the overall reverse reaction rate constant, K_r is not sensitive to the acidity of the solution. This may be due to the opposite effect of acidity on the reverse steps of Equations (20) and (23).

Comparing Equations (26) and (33) we obtain

$$k_1 = 90.15 \qquad M^{-1}\ sec^{-1} \tag{35}$$

and

$$k_2K_h + k_3K_{HA} + k_4K_h = 0.0734 \qquad sec^{-1} \tag{36}$$

Since the equilibrium concentrations of oxine anion (A^-), is much less than (about 10^{-6}M) that of the undissociated oxine, (HA), in aqueous solution (13), the reaction pathes of (22) and (23) may be not so important as those of (20) and (21). Under this proposition Equation (36) may be simplified further to

$$k_2K_h = 0.0734 \qquad sec^{-1} \tag{37}$$

The value of K_h at ionic strength of 0.1 may be obtained as 6.195 x 10^{-3}M (14) and then k_2 can be calculated as 11.84 $M^{-1}sec^{-1}$. This result indicates that k_1 and k_2 values are in the same order, while k_1 is larger than k_2.

From the stereo structures of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5(OH)^{2+}$, symmetry is not quite different, because the OH^- size is about the same as the H_2O molecule. However, Fe^{3+} drawing the electron pairs of ligand is stronger than that of $Fe(OH)^{2+}$. Therefore, this may explain why k_1 is larger than k_2.

CONCLUSION

The complexation reactions of ferric iron with oxine and KELEX-100 are first order with respect to both Fe^{3+} and legand concentrations. The observed rate law indicates inverse-first-order with respect to hydrogen ion in aqueous solution. Experimental results indicate the reaction pathes with the formation of the first complex from either Fe^{3+} or $Fe(OH)^{2+}$ with HA is predominent. The first step reaction path from Fe^{3+} may react faster than the second step reaction path from $Fe(OH)^{2+}$.

NOMENCLATURE

A = Absorbance or optical density
ΔE = Activation energy
K = Equilibrium constant
k = Reaction rate constant
M = Molar concentration
R = Gas constant
T = Temperature
t = Time
σ = Standard deviation
M = Ionic strength

Subscript

o = initial
∞ = equilibrium
1 = first step forward reaction
-1 = first step backward reaction
h = hydrolysis
f = forward reaction
r = backward reaction

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