Polarographic Study of the Rate of Oxidation of Iron(II) Chelates by Hydrogen Peroxide

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Considerable interest is being paid to the structure of aminocarboxylic acid complexes of the bivalent transition metal ions in aqueous solution. EDTA (ethylenediamine-N,N,N',N'-tetraacetic acid) is known to act as a quinquadentate ligand and, depending on the pH of the solution, with Co(II) and Ni(II) as a sexadentate ligand.[1-3] HEDTA (N-(2-hydroxyethyl)-ethylenediamine-N,N',N'-triacetic acid) is assumed to act as a quinquadentate ligand with Co(II)[2] while NTA (nitrilotriacetic acid) has a maximum chelation number of four in the 1:1 complexes. Very little is known in the case of Fe(II) aminocarboxylate complexes.

The rate of oxidation of a complexed metal ion will depend on protonation of the complex.[4] So, from an examination of the pH dependence of the redox reaction, information about the structure of the complex can be obtained. This note reports the results obtained by a polarographic investigation of the oxidation rate of Fe(II)-EDTA, -HEDTA, and -NTA complexes. The oxidant was hydrogen peroxide.

The reactions to be considered are the following

$$Fe(III) + e^- \rightleftharpoons Fe(II) \tag{1}$$

$$Fe(II) + H_2O_2 \xrightarrow{k} Fe(III) + \cdot OH + OH^- \tag{2}$$
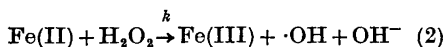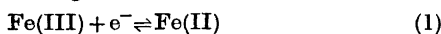
Fe(II) and Fe(III) represent all the ferrous and ferric species, respectively. The polarographic reduction (1) occurs reversibly. In order to avoid further reactions acrylonitrile was added as a scavenger to remove the $\cdot OH$ radicals.

The diffusion current i_d of hydrogen peroxide was read directly from the polarogram. The limiting current i_{lim} in the reaction mixture was measured as the distance from the base line to the intersection of a line through the middle points of the oscillations at the plateau and a

vertical line through the Fe(III)/Fe(II) half-wave potential.

In order to determine the rate constants, the conditions under which i_{lim} is solely kinetically controlled must be applied. From the dependence of the limiting current on the height of the mercury column the current was found to be kinetically controlled when the ratio of hydrogen peroxide to iron(III) was greater than 18. This ratio was sustained throughout all experiments.

The polarographic experiments were carried out in buffered solutions in the pH-range $0-6.5$ and the rate constants were calculated using a modified form of the Brdička-Wiesner equation[5] which, under the present conditions, agrees within a few percent with Koutecky's exact solution.[6]

When z different Fe(II) species react with hydrogen peroxide the following equation applies:

$$y = \frac{I}{(1/I)-1} = 0.660 \frac{\alpha n_1^2}{n_2^2} t_1 \frac{D_{Fe(II)}}{D_{H_2O_2}}$$
$$\left\{ \sum_{i=1}^{i=z} (\sqrt{k_i}\, [Fe(II)_i]) \right\}^2 \frac{1}{[H_2O_2]}$$

where $I = i_{lim}/(i_d)$ and n_1 and n_2 are the numbers of electrons involved in the reduction of an Fe(III) species and a hydrogen peroxide molecule, (in this case $n_1 = 1$ and $n_2 = 2$). t_1 is the drop time, $D_{H_2O_2}$ and $D_{Fe(II)}$ are the diffusion coefficients, α is the number of Fe(II) species being oxidised by one molecule of H_2O_2. From reaction (2) it is seen that α is 1. k_i is the rate constant of the i'th Fe(II) species. The concentrations of the various Fe(II) complexes as a function of pH were calculated from the stability constants.[7] The stability constants of the protonated complexes are, with the exception of the monoprotonated Fe(II)-EDTA complex at 20°C,[7] not known, and were therefore treated as unknowns together with the rate constants.

In order to explain an observed decrease in reactivity at pH $> ca.$ 6 in the case of Fe(II)-NTA, the existence of an inactive 1:2 complex was assumed. A 1:2 complex has earlier been proposed by Schwarzenbach and Heller.[8]

The calculations were carried out by means of a GIER computer. A program for minimising $\sum(y_{obs} - y_{calc})^2$ as a function of the rate constants and the stability constants of the protonated complexes was written in GIER ALGOL 4 using the

Table 1. The rate constants at different temperatures together with the activation energy and activation entropy. Ionic strength= 0.20.

Fe(II) aqua	Rate constant $M^{-1}sec^{-1}$	Temp. °C				E_{act} kcal	$\Delta S^{\ddagger}$ cal/K
		10.0	20.0	30.0	40.0		
	$k_{(Fe^{2+})}$	37 ± 4	60 ± 6	108 ± 8	167 ± 13	9.1 ± 0.4	-21 ± 2
EDTA	$k_{(FeH_2Y)} \times 10^{-4}$	2.0 ± 0.5	4.0 ± 0.6	5.0 ± 1.0	7.9 ± 0.7	7.7 ± 0.4	-13 ± 4
	$k_{(FeHY^-)} \times 10^{-4}$	2.8 ± 0.2	3.86 ± 0.09	6.0 ± 0.3	7.53 ± 0.01	6.6 ± 0.4	-17 ± 2
	$k_{(FeY^{2-})} \times 10^{-4}$	0.57 ± 0.01	0.910 ± 0.008	1.22 ± 0.07	1.67 ± 0.09	6.5 ± 0.3	-21 ± 2
HEDTA	$k_{(FeHY)} \times 10^{-4}$	1.51 ± 0.02	2.77 ± 0.08	4.6 ± 0.2	6.4 ± 0.1	8.6 ± 0.6	-11 ± 2
	$k_{(FeY^-)} \times 10^{-4}$	0.976 ± 0.006	1.67 ± 0.01	2.52 ± 0.07	3.54 ± 0.03	7.5 ± 0.6	-15 ± 2
NTA	$k_{(FeHY)} \times 10^{-4}$	4 ± 4	6 ± 6	2.0 ± 0.9	4.1 ± 0.6		
	$k_{(FeY^-)} \times 10^{-4}$	1.33 ± 0.05	1.84 ± 0.01	2.86 ± 0.06	4.07 ± 0.02	6.7 ± 0.7	-17 ± 2

Table 2. The stability constants at different temperatures together with the enthalpy and entropy of formation. Ionic strength= 0.20.

Ligand	EDTA		HEDTA	NTA	
Temp. °C	K_{FeH_2Y}	K_{FeHY^-}	K_{FeHY}	K_{FeHY}	$K_{FeY_2^{-}}$
10.0	$(2.4 \pm 0.4)10^3$	$(8.0 \pm 0.2)10^6$	$(1.4 \pm 0.2)10^5$	10 ± 5	$(2.0 \pm 0.8)10^4$
20.0	$(1.8 \pm 0.4)10^3$	$(8.0 \pm 0.1)10^6$	$(1.3 \pm 0.2)10^5$	9 ± 7	$(1.0 \pm 0.5)10^4$
30.0	$(2.5 \pm 0.8)10^3$	$(6.7 \pm 0.3)10^6$	$(1.2 \pm 0.3)10^5$	16 ± 12	$(9 \pm 4)10^3$
40.0	$(2.2 \pm 1.2)10^3$	$(7.4 \pm 0.1)10^6$	$(1.2 \pm 0.1)10^5$	150 ± 20	$(9 \pm 3)10^3$
ΔH° kcal		-0.7 ± 0.3	-0.8 ± 0.3		
ΔS° cal/K		29 ± 4	21 ± 3		

LETAGROP procedure.[9] Table 1 shows the calculated rate constants, activation energies, and activation entropies, while Table 2 contains the stability constants, enthalpies, and entropies of formation. The results of the reaction between the Fe^{2+}(aq)

ion and hydrogen peroxide are in good agreement with the literature [20] as is the stability constant of the monoprotonated Fe(II)-EDTA complex at 20°C.[7]

The tables clearly show the existence of a mono-, a di-, and an unprotonated

complex with EDTA. With HEDTA only a
mono- and an unprotonated complex seem
to exist while the existence of a protonated
NTA complex is rather doubtful. Table 1
demonstrates a striking difference in
reactivity between the unprotonated and
the two protonated Fe(II)-EDTA com-
plexes. This may be due to an equilibrium
between sexa- and quinquadentate bound
ligand, the former being less reactive, as the
reaction involves the breaking of a metal-
carboxylate bond.

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A Method for Solubility Measurements in a Two Phase Liquid System

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Solubility measurements at high tem-
peratures in molten systems where the
solubility changes with temperature is
often very difficult to perform. A common
method is to freeze the equilibrium by a
rapid quench and then analyse the solidi-
fied phases. Great care must be exercised,
however, in order to obtain the true values
as the composition of the melt usually
changes very rapidly during quenching.
This is particularly the case in those metal/
molten salt systems where the metal has a
high vapour pressure and the molten salt
phase a relatively low heat conductivity.
A further complication is the fact that
these salts normally supercool very easily.

If a two phase equilibrium mixture of a
metal-metal salt system is rapidly quenched
from a high temperature the metal dis-
solved in the salt phase will precipitate out
of that phase and to some extent join the
metal phase. This is, *e.g.*, the case in the
$Ca-CaCl_2$ system where the metal is much
lighter than the salt and consequently
floats on top of the latter. This system ex-
hibits a large miscibility gap that closes
at 1338°C.[1] Experiments in this system
have shown that a mixture of metal and
salt with an overall composition in the two
phase region after equilibration at 1100°C
in a closed iron crucible changes its salt
phase composition due to precipitation of
metal from the salt solution even during a
very rapid quench in brine. Subsequent
chemical analysis of the phases from the
quenched sample did therefore not give
the true high temperature equilibrium
values but instead it was found that the
solubility figure for the metal varied
depending on the quenching rate and from
which part of the salt phase the sample was
taken.

If mass transfer between the two phases
in some way could be prevented after
equilibrium was reached true values of the
solubility of the metal could be obtained
by analysing the whole of the salt phase.