INDIVIDUAL QUANTUM YIELDS OF $Fe^{3+}OX_n^{2-}H_m^+$ COMPLEXES IN AQUEOUS ACIDIC SOLUTIONS ($OX^{2-} \equiv C_2O_4^{2-}$, $n = 1 \cdot 3$, $m = 0,1$)

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Summary

The following molar absorbancies and individual quantum yields (IQYs) of iron(III)–oxalate complexes were determined at 254 nm, taking into consideration the uncertainties of the stability constants: $\epsilon(Fe^{3+}OX^{2-}) = 2750 \pm 160$ M^{-1} cm^{-1}; $\epsilon(Fe^{3+}OX_2^{2-}) = 4400 \pm 300$ M^{-1} cm^{-1}; $\epsilon(Fe^{3+}OX_3^{2-}) = 7170 \pm 460$ M^{-1} cm^{-1}; $\epsilon(Fe^{3+}OX^{2-}H^+) = 5130 \pm 80$ M^{-1} cm^{-1}; $\Phi(Fe^{3+}OX^{2-}) = 0$; $\Phi(Fe^{3+}OX_2^{2-}) = 0.59 \pm 0.03$; $\Phi(Fe^{3+}OX_3^{2-}) = 0.80 \pm 0.03$; $\Phi(Fe^{3+}OX^{2-}H^+) = 0.82 \pm 0.02$.

The dependence of IQYs on the number of coordinated oxalate ligands is discussed.

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1. Introduction

Potassium ferrioxalate is one of the most widely used actinometers and has already been investigated by several researchers. Since the work of Parker and Hatchard [1 - 3] the sources of errors have been analysed [4 - 6], the actinometric method has been developed [7 - 15] and the mechanism of the reaction has been investigated by flash photolysis [16 - 21]. The individual quantum yields (IQYs) of the different iron(III)–oxalate complexes have not yet been reported.

Our aim was to obtain these values by systematically performing experiments over a wide range of concentrations. We wished to clarify if there is any measurable concentration dependence, contrary to the findings of Parker and Hatchard [1, 2]. The uncertainties were properly taken into consideration. All the computed values were compared with the corresponding measured data.

2. Experimental details

The irradiations were carried out using a low pressure mercury vapour lamp (Voltarc UV LUX TM OT5, Applied Photophysics), with a $CoSO_4^-$

$NiSO_4$ filter solution. The samples were contained in a quartz cuvette of optical path 0.5 cm and were purged with argon.

The $FeCl_3$, $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$, $C_2O_4K_2 \cdot H_2O$ (Reanal) and H_2SO_4 (Carlo−Erba) were analytical grade and the argon was a commercial product. The traces of oxygen were removed from the argon by a BASF-R3-11 catalyst, and the other chemicals were used without further purification. All solutions were made with doubly distilled water. The K_3FeOX_3 (OX $\equiv$ $C_2O_4^{2-}$) was prepared according to the method given in ref. 1.

The iron(II) formed from the photoreduction was estimated by using *ortho*-phenanthroline which was also protected from light [5]. UV−visible spectra were recorded with a Specord UV−visible spectrophotometer (Carl Zeiss, Jena).

The molar absorbancies of $FeOX_nH_m$ species were determined by using 2×10^{-4} M iron(III), and the concentrations of $C_2O_4K_2$ and H_2SO_4 were 10^{-5} M, 10^{-4} M, 10^{-3} M, 10^{-2} M and 0.01 M, 0.05 M, 0.1 M, 0.2 M, 0.5 M respectively. Altogether, 20 solutions were prepared. The photoreduction was studied with acidic K_3FeOX_3 solutions. The concentration of K_3FeOX_3 was varied over the range 10^{-4} - (2×10^{-2}) M with two concentrations (0.05 and 0.5 M) of H_2SO_4. For the computation of the molar absorbancies of OX^{2-}, OXH^- and OXH_2 the spectra of 5×10^{-3} M $C_2O_4K_2$ were recorded at eight different H_2SO_4 concentrations. The details of our computation procedure are given in ref. 22. The composition matrix for the complexes and the stability constants are the input for the computations. These are collected in Table 1. The stability constants and their assumed deviations were obtained by analysing the literature data. The method is described elsewhere [23].

TABLE 1

Composition matrix of the iron(III)−oxalate system in sulphuric acid, and the stability constants at zero ionic strength

Complex	Components				$\lg \beta_t$
	Fe^{3+}	$C_2O_4^{2-}$	SO_4^{2-}	H^+	
$Fe^{3+}C_2O_4^{2-}$	1	1	0	0	9.40 ± 0.06
$Fe^{3+}(C_2O_4^{2-})_2$	1	2	0	0	16.20 ± 0.45
$Fe^{3+}(C_2O_4^{2-})_3$	1	3	0	0	20.78 ± 0.90
$Fe^{3+}C_2O_4^{2-}H^+$	1	1	0	1	9.53 ± 0.6
$Fe^{3+}SO_4^{2-}$	1	0	1	0	4.05 ± 0.12
$Fe^{3+}(SO_4^{2-})_2$	1	0	2	0	5.57 ± 0.64
$Fe^{3+}SO_4^{2-}H^+$	1	0	1	1	2.83 ± 0.87
$Fe^{3+}(SO_4^{2-})_2H^+$	1	0	2	1	6.55 ± 0.6
$C_2O_4^{2-}H^+$	0	1	0	1	4.21 ± 0.07
$C_2O_4^{2-}(H^+)_2$	0	1	0	2	5.65 ± 0.15
$H^+SO_4^{2-}$	0	0	1	1	1.96 ± 0.10

3. Results and discussion

The mole-ratio distributions of iron(III) species at different H_2SO_4 concentrations are shown in Figs. 1 and 2. In these figures the effect of the deviation of $\beta(Fe^{3+}OX_3^{2-})$ is also shown, where β is the complex stability constant. The absorbancies, the pHs and the concentrations of free oxalate ions in the solutions prepared for the molar absorbancy computations are collected in Table 2.

For the computation of the molar absorbancies of iron(III)–oxalate complexes those of the OX^{2-}, OXH^- and OXH_2 species must be known, as

Fig. 1. Mole-ratio distribution of the iron(III)–oxalate complexes in 0.05 M sulphuric acid solutions (pH 1.25), and its dependence on the stability constant of the Fe^{3+}-$(C_2O_4^{2-})_3$ species.
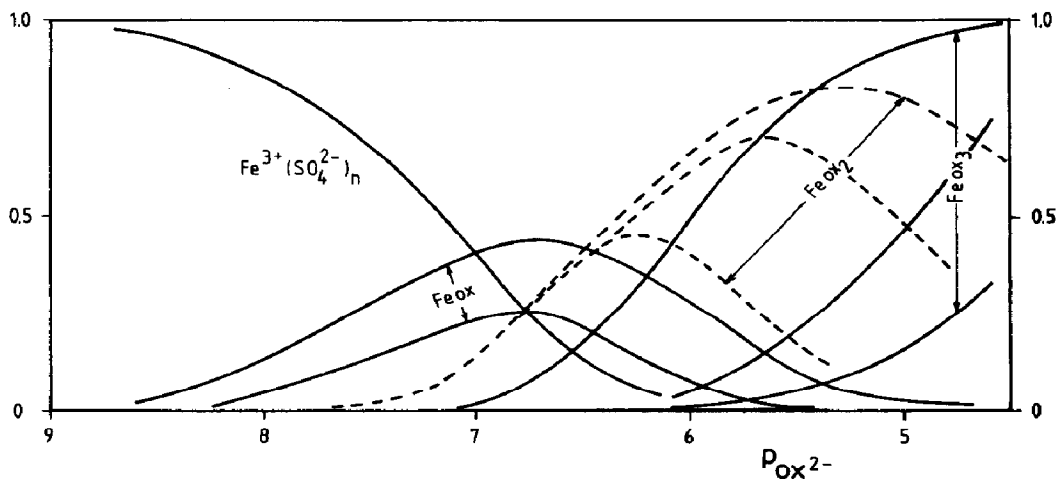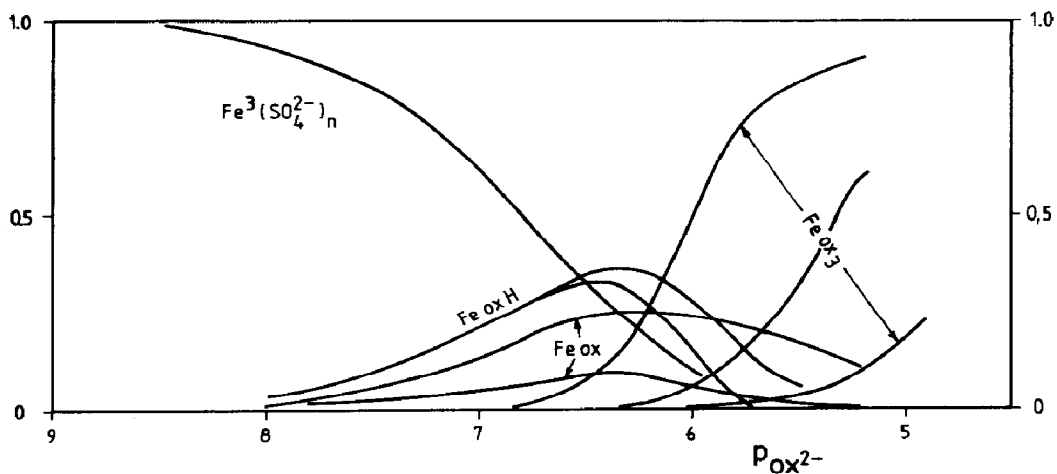

Fig. 2. Mole-ratio distribution of the iron(III)–oxalate complexes in 0.50 M sulphuric acid solutions (pH 0.29), and its dependence on the stability constant of the Fe^{3+}-$(C_2O_4^{2-})_3$ species.

TABLE 2

Solutions made for the determination of the molar absorbancies of the iron(III)–oxalate species at 254 nm

	Analytical concentration (M)			$10^6[C_2O_4^{2-}]^a$ (M)			pH	A/d
	$C_2O_4K_2$	$Fe(III)$	H_2SO_4	A	B	C		
1	10^{-5}	1.98×10^{-4}	0.01	0.003	0.0015	0.0014	1.85	0.605
2	10^{-5}	1.98×10^{-4}	0.05	0.0056	0.0032	0.0029	1.23	0.578
3	10^{-5}	1.98×10^{-4}	0.10	0.0043	0.0029	0.0028	0.95	0.571
4	10^{-5}	1.98×10^{-4}	0.20	0.0024	0.0019	0.0018	0.67	0.624
5	10^{-5}	1.98×10^{-4}	0.50	0.0007	0.0006	0.0006	0.29	0.629
6	10^{-4}	1.8×10^{-4}	0.01	0.036	0.0245	0.0232	1.89	0.530
7	10^{-4}	1.8×10^{-4}	0.05	0.056	0.0402	0.0378	1.27	0.537
8	10^{-4}	1.8×10^{-4}	0.10	0.046	0.0342	0.0327	0.99	0.523
9	10^{-4}	1.8×10^{-4}	0.20	0.027	0.0212	0.0207	0.71	0.579
10	10^{-4}	1.8×10^{-4}	0.50	0.0083	0.0067	0.0069	0.33	0.576
11	10^{-3}	1.98×10^{-4}	0.01	3.292	3.342	3.529	1.87	0.907
12	10^{-3}	1.98×10^{-4}	0.05	0.817	0.818	0.828	1.24	0.872
13	10^{-3}	1.98×10^{-4}	0.10	0.454	0.431	0.432	0.95	0.737
14	10^{-3}	1.98×10^{-4}	0.20	0.243	0.21	0.209	0.67	0.764
15	10^{-3}	1.98×10^{-4}	0.50	0.072	0.060	0.0597	0.29	0.696
16	10^{-2}	1.8×10^{-4}	0.01	230.9	177.4	179.7	2.25	1.764
17	10^{-2}	1.8×10^{-4}	0.05	22.68	17.89	18.03	1.37	1.463
18	10^{-2}	1.8×10^{-4}	0.10	9.30	7.506	7.556	1.05	1.329
19	10^{-2}	1.8×10^{-4}	0.20	3.66	3.033	3.044	0.74	1.285
20	10^{-2}	1.8×10^{-4}	0.50	0.92	0.772	0.772	0.34	1.115

[a]A, $\log \beta_t\{Fe^{3+}(C_2O_4^{2-})_3\} = 21.68$; B, $\log \beta_t\{Fe^{3+}(C_2O_4^{2-})_3\} = 20.78$; C, $\log \beta_t\{Fe^{3+}(C_2O_4^{2-})_3\} = 19.88$.

their light absorption is not negligible at 254 nm. The calculated concentration distributions and the absorbancies computed for protonated oxalate ions are given in Table 3. The results are in accordance with those of Cruywagen and Heyus [24], who were the first to publish a detailed investigation of this system. The data of Morozova [25] and Szyper and Zuman [26] concern selected wavelengths only.

The average molar absorbancy was taken into consideration for the iron(III)–sulphate species. The computed molar absorbancies of $FeOX_nH_m$ are given in Table 4. Deviations are assigned to the molar absorbancies as the stability constants are also probability variables. The measured and calculated absorbancies are compared in Fig. 3; it can be seen that the fit is quite good. The fit is best for $\lg \beta(Fe^{3+}OX_3^{2-}) = 19.88$, suggesting that this value may be the closest to the true one.

The experimental and individual quantum yields were computed according to the method described in ref. 22. The experimental quantum

TABLE 3

Solutions made for the computation of the molar absorbancies of $C_2O_4^{2-}$, $C_2O_4H^-$ and $C_2O_4H_2$ at 254 nm

	Analytical concentration (M)		10^6C (M)			A/d	
	$C_2O_4K_2$	H_2SO_4	$C_2O_4^{2-}$	$C_2O_4H^-$	$C_2O_4H_2$	Measured	Computed
1	0.005	0.5	0.318	624.1	4367	0.202	0.199
2	0.005	0.2	1.276	1205	3784	0.209	0.212
3	0.005	0.1	3.106	1807	3198	0.223	0.227
4	0.005	0.05	6.996	2509	2496	0.241	0.243
5	0.005	0.02	19.62	3464	1526	0.265	0.264
6	0.005	0.01	44.52	4087	877.6	0.279	0.278
7	0.005	0.005	123.2	4519	368.6	0.288	0.286
8	0.005	0.002	1312	3658	21.97	0.249	0.248
9	0.005	0.001	3064	1924	2.616	0.179	0.181
10	0.005	0.0	4999	1.09	0.0	0.108	0.108

$\epsilon_{C_2O_4} = 21.6\ M^{-1}\ cm^{-1}$; $\epsilon_{C_2O_4H} = 59.7\ M^{-1}\ cm^{-1}$; $\epsilon_{C_2O_4H_2} = 37.1\ M^{-1}\ cm^{-1}$.

TABLE 4

Molar absorbancies and individual quantum yields of the iron(III)–oxalate–sulphate system at 254 nm

Complex	$10^{-3}\epsilon$ ($M^{-1}\ cm^{-1}$)	Quantum yield
$Fe^{3+}C_2O_4^{2-}$	2.75 ± 0.16	0
$Fe^{3+}(C_2O_4^{2-})_2$	4.40 ± 0.30	0.59 ± 0.03
$Fe^{3+}(C_2O_4^{2-})_3$	7.17 ± 0.46	0.80 ± 0.03
$Fe^{3+}C_2O_4^{2-}H^+$	5.13 ± 0.08	0.82 ± 0.02
$Fe^{3+}(SO_4^{2-})_nH_m$	3.04 ± 0.01	0.0

yields of all the solutions are collected in Table 5; the IQYs are given in Table 4. The experimental and the individual quantum yields are compared in Fig. 4. The relatively low value of the IQY of the species $Fe^{3+}OX^{2-}$ can be interpreted in terms of the lack of other oxalato ligands in the coordination sphere which could help dissipate the excitation energy after the photoreduction. The stabilization of Co^{2+} ions after the photoreduction of Co^{3+}-$(NH_3)_5L$ complexes is also assisted by the dissipation of excess excitation energy via dissociation of ligands [27].
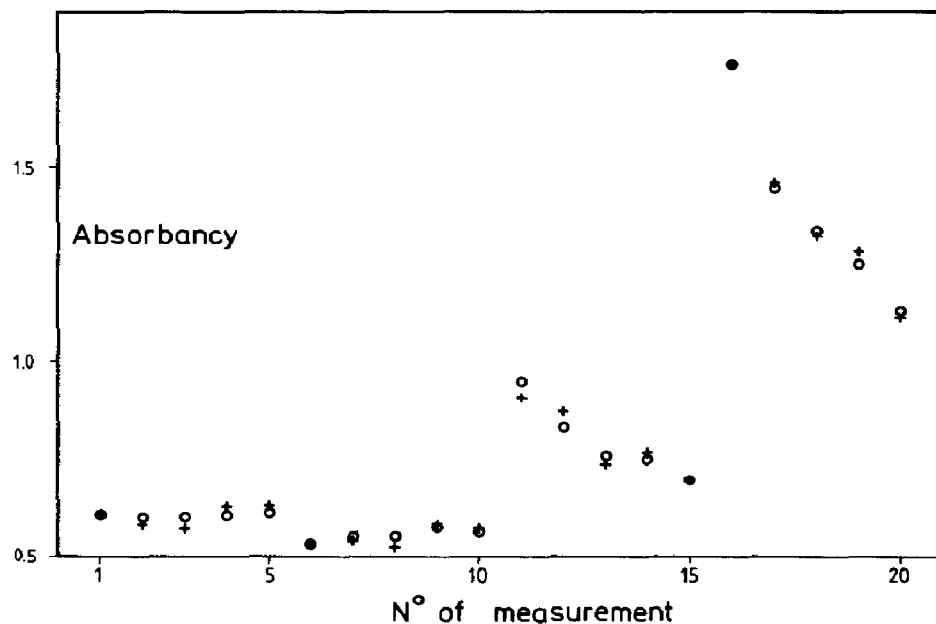
Fig. 3. Measured (+) and calculated (○) absorbancies of iron(III)–oxalate solutions (see Table 2).

TABLE 5

Experimental quantum yields of the iron(III)–oxalate systems

|	Analytical concentration (M)		$P_{C_2O_4^{2-}}$	Experimental quantum yield
	$K_3[Fe(C_2O_4)_3]$	H_2SO_4		
1	0.0004	0.05	6.16	0.43
2	0.0006	0.05	6.02	0.48
3	0.0010	0.05	5.85	0.49
4	0.0012	0.05	5.78	0.48
5	0.0024	0.05	5.55	0.62
6	0.0036	0.05	5.40	0.64
7	0.0050	0.05	5.29	0.575
8	0.0060	0.05	5.23	0.615
9	0.010	0.05	5.05	0.64
10	0.020	0.05	4.83	0.65
11	0.040	0.05	4.63	0.79
12	0.0004	0.50	7.17	0.12
13	0.0006	0.50	7.01	0.19
14	0.0010	0.50	6.81	0.21
15	0.0012	0.50	6.74	0.32
16	0.0024	0.50	6.47	0.48
17	0.0036	0.50	6.32	0.55
18	0.0050	0.50	6.20	0.53
19	0.0060	0.50	6.13	0.58
20	0.010	0.50	5.95	0.55
21	0.020	0.50	5.71	0.67
22	0.040	0.50	5.49	0.75
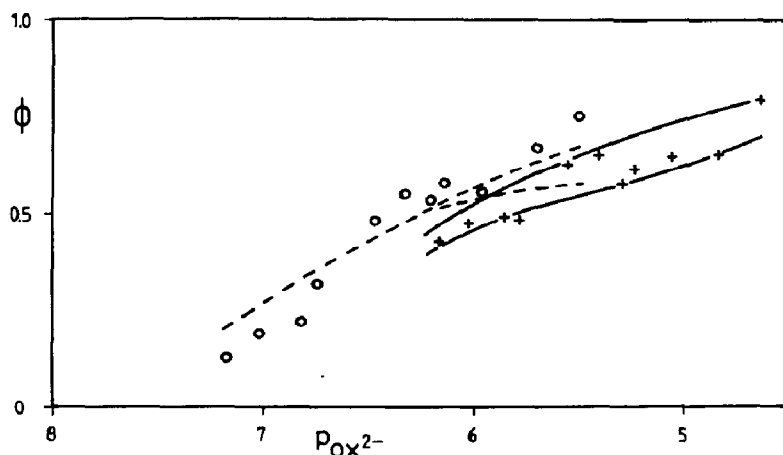
Fig. 4. Quantum yields found and calculated for iron(III)–oxalate complexes in aqueous acidic solutions. $\bigcirc$ and $+$, found at pH 0.29 and 1.25 respectively; $-\,-\,-$ and $-\!-\!-$, calculated at pH 0.29 and 1.25 respectively, considering the mole-ratio distribution alternatives.

4. Conclusions

According to the published literature, the $Fe^{3+}OX_n{}^{2-}H_m$ complexes have identical IQYs. However, the experimental quantum yield of the aqueous acidic iron(III)–oxalate system depends on the composition. The extent of the dependence exceeds the experimental error, and the measured results can be interpreted in terms of IQYs of the various complexes. The increase in the IQYs with the extent of complexation can be interpreted in terms of increased dissipation of the excess excitation energy by the excess ligands of the complex.

Acknowledgment

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Appendix A: Nomenclature

A absorbance
d optical path (cm)
β complex stability constant
ϵ molar absorbance ($M^{-1}\,cm^{-1}$)
Φ individual quantum yield