

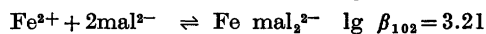
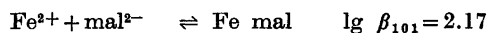
Thermodynamic Properties of Iron Oxalates and Malonates in Perchlorate Medium

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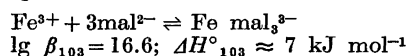
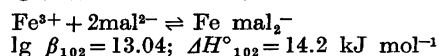
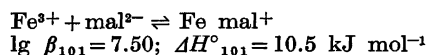
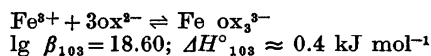
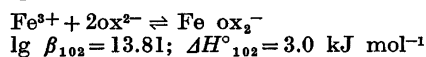
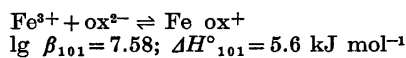
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Potentiometric measurements at ionic strength 1 M (NaClO₄) and at 25.0 °C have been made to determine the stability constants for the Fe³⁺ malonate complexes, the Fe³⁺ oxalate, and Fe³⁺ malonate complexes. The enthalpies of formation of the ferric oxalate and malonate complexes have been determined calorimetrically.

The Fe²⁺ malonate system was investigated by means of a glass electrode, and equilibrium constants were obtained for the following reactions:



From redox-potential and calorimetric measurements, the following overall equilibrium constants and enthalpy values were calculated:



The complex formation reactions in aqueous solution between iron(II or III) ion and organic ligands derived from saturated mono- or dicarboxylic acids have not been characterized in a satisfactory way. The entries in a comprehensive compilation such as Stability Constants¹ show that several investigations have

resulted in discordant interpretations as to which species that are formed and their stability constants. The main reason for the inconsistent results obtained is probably the complications introduced by the hydrolysis of Fe³⁺ (aq) ion, which makes the interpretation of experimental data difficult.

The ferric ion oxalate system has been the subject of several investigations.²⁻⁶ Deneux *et al.*² have determined stability constants for the complexes Fe(C₂O₄)_n³⁻²ⁿ, where n = 1, 2, and 3. The existence of a hydrogen oxalate complex, FeHC₂O₄²⁺, has been reported once,³ but its formation is questioned by other investigators.^{2,4,5} Several determinations of β₁, the stability constant for the monooxalato complex, are in fair agreement with each other.^{2,4-6} However, values for β₂ and β₃ that differ with about a factor of ten, are reported.^{2,6} In order to resolve these discrepancies, the Fe³⁺ oxalate system was reinvestigated.

The investigations of Deneux *et al.*² and Gordienko *et al.*⁵ disagree upon the malonate system. Deneux *et al.* report a stability constant for the formation of the first malonate complex that is only about 10 % smaller than the corresponding constant for the oxalate system. The trivalent rare earth ion complexes with oxalate ion are more stable than the malonate complexes with a factor of about 20.^{7,8} The values reported by Gordienko *et al.* for the corresponding Fe³⁺ ion complexes follow this pattern, but these investigators also found that the protonated complex FeHCH₂(COO)₂²⁺ is formed in substantial amounts; it would be the dominating ferric

ion complex in the concentration range investigated by Deneux *et al.* Thus, another study of this system is desirable.

In order to calculate stability constants for ferric ion complexes from emf measurements on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, the stability constants for the corresponding ferrous ion complexes must be known. The Fe^{2+} oxalate system has been studied by Bottari and Ciavatta,⁹ but no accurate data on Fe^{2+} malonate complexes were available. This system has been investigated here.

There is a nearly complete lack of calorimetric data for complex formation reactions between ferric ion and carboxylate ligands of the type discussed here. Uri¹⁰ has reported $K = 3 \times 10^9 \text{ M}^{-1}$ and $\Delta H^\circ = -0.3 \text{ kcal mol}^{-1}$ for the formation of the monooxalato iron(III) complex, but it is not stated under which conditions these values are supposed to be valid. The enthalpies of formation of the complexes formed in the Fe^{3+} oxalate and malonate systems therefore have been determined.

NOTATIONS

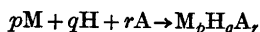
C_M , C_H , and C_A denote the total concentrations of metal ion, free and dissociable hydrogen ions, and ligand ion (oxalate or malonate) respectively. The concentration of free metal ion, hydrogen ion, and ligand ion are denoted m , h , and a , respectively. Ionic charges are usually omitted.

β_{pqr} = the overall stability constant for the complex $\text{M}_p\text{H}_q\text{A}_r$, defined as

$$\beta_{pqr} = [\text{M}_p\text{H}_q\text{A}_r] m^{-p} h^{-q} a^{-r}$$

$$\bar{n} = (C_A - \sum_{j=0}^2 [\text{H}_j\text{A}]) / C_M$$

ΔH°_{pqr} = the standard enthalpy change for the reaction



V = the total volume of the system, $V = V_0 + v$
 V_0 = the initial volume of the titrand solution, S ,
 v = the added volume of the titrator solution, T ,
 Q = the enthalpy change at the addition of T solution.

EXPERIMENTAL

Chemicals used. $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (Schuchardt, *p.a.*) and $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (Carl Roth, recrystallized from dilute HClO_4), were used for the preparation of the metal ion solutions. The ferrous perchlorate sample contained about 1 % iron as $\text{Fe}(\text{III})$. Stock solutions of $\text{Fe}(\text{ClO}_4)_3$ were reduced with H_2S prior to use, after which treatment $[\text{Fe}(\text{III})] \leq 2 \times 10^{-5} \text{ M}$, as estimated from the reaction with KSCN solution. The iron content was determined by titration with KMnO_4 and the hydrogen ion content by a cation exchange procedure. All other chemicals used were of reagent grade and purified prior to use, when necessary. The measurements were made under nitrogen, which had passed through wash bottles with a $\text{Cr}(\text{II})$ solution and 1 M NaClO_4 .

Potentiometric measurements. The emf E of galvanic cells of the types given in Scheme 1 were measured. (A denotes either oxalate or malonate ion). In addition, sodium perchlorate was added to the solutions to make the total concentration of ionic equivalents, $I' = \frac{1}{2} (\sum c_i |z_i|)$, equal to 1.00 M. (As the concentration of polyvalent ions was rather low, also the formal ionic strength, $I = \frac{1}{2} (\sum c_i z_i^2)$, is close to 1.00 M). The pH measurements on the Fe^{3+} malonate system were made with a Jena glass electrode of the "Thalamid" type, while a bright platinum foil (area $\sim 11 \text{ cm}^2$) was used in the redox measurements. The Ag, AgCl electrodes were prepared according to Brown.¹¹ The emf values were measured to 0.1 mV with a digital Orion 801 voltmeter. The reproducibility of the emf values was usually within 0.2 mV. However, the last points of series 3, Table 1, were only reproducible to within 0.5 mV. The equilibration time for these points was also considerably longer (5–20 min) than for the other points, which equilibrated practically instantaneously. This might be caused by hydrolysis, due to a local excess of the titrator and subsequent slow equilibration of the hydrolyzed species. The final solutions are stable and remain clear for at least several

Ag, AgCl (s)	0.02500 M	1.00 M	$C_{\text{Fe}^{3+}}$	$\text{Fe}(\text{ClO}_4)_3$	Glass electrode or Pt (s)
	NaCl		$C_{\text{Fe}^{2+}}$	$\text{Fe}(\text{ClO}_4)_2$	
	0.975 M	NaClO ₄	$C_{\text{H}_2\text{A}}$	H_2A	
	NaClO ₄		$C_{\text{Na}_2\text{A}}$	Na_2A	
				C_{HClO_4}	

Scheme 1.

Table 1. Some experimental data for the Fe^{3+} malonate system. The results are given as v/ml , E/mV . The S and T solutions contain sodium perchlorate to make the total concentration of ionic equivalents equal to 1.00 M.

Series 1. S: $C_{\text{H}} = 148.5 \text{ mM}$, $C_{\text{Fe(III)}} = 5.88 \text{ mM}$, $C_{\text{Fe(II)}} = 5.26 \text{ mM}$, $C_{\text{A}} = 0$; T: $C_{\text{H}} = 338.0 \text{ mM}$, $C_{\text{Fe(III)}} = 5.88 \text{ mM}$, $C_{\text{Fe(II)}} = 5.26 \text{ mM}$, $C_{\text{A}} = 99.62 \text{ mM}$; $V_0 = 21 \text{ ml}$, $E_0 = 402.7 \text{ mV}$.

0.25, 404.5; 1, 402.5; 2, 400.1; 3.5, 397.1; 5, 394.7; 7, 392.1; 9, 390.0; 11.5, 387.8; 15, 385.6; 17, 384.5; 22, 382.4.

Series 2. S: $C_{\text{H}} = 148.5 \text{ mM}$, $C_{\text{Fe(III)}} = 12.35 \text{ mM}$, $C_{\text{Fe(II)}} = 11.21 \text{ mM}$, $C_{\text{A}} = 0$; T: $C_{\text{H}} = 419.3 \text{ mM}$, $C_{\text{Fe(III)}} = 12.35 \text{ mM}$, $C_{\text{Fe(II)}} = 11.21 \text{ mM}$, $C_{\text{A}} = 149.6 \text{ mM}$; $V_0 = 25 \text{ ml}$, $E_0 = 401.3 \text{ mV}$.

0.5, 402.2; 1, 400.6; 1.5, 399.2; 2, 397.8; 3.25, 394.9; 5, 391.6; 7, 388.5; 9.5, 385.5; 11, 384.0; 14, 381.4; 18, 378.8; 24, 375.8.

Series 3. S: $C_{\text{H}} = 33.30 \text{ mM}$, $C_{\text{Fe(III)}} = 3.430 \text{ mM}$, $C_{\text{Fe(II)}} = 3.115 \text{ mM}$, $C_{\text{A}} = 0$; T: $C_{\text{H}} = 99.2 \text{ mM}$, $C_{\text{Fe(III)}} = C_{\text{Fe(II)}} = 0$, $C_{\text{A}} = 99.6 \text{ mM}$; $V_0 = 24 \text{ ml}$, $E_0 = 410.4 \text{ mV}$.

0.2, 407.4; 0.6, 398.8; 1, 390.2; 1.5, 380.1; 2, 370.7; 2.6, 360.3; 3.4, 347.5; 4.2, 335.4; 5, 323.6; 5.8, 311.8; 6.6, 300.1; 7.5, 286.6; 8.5, 271.2; 9.5, 255.2; 10.75, 235.3; 12.25, 212.1; 13.5, 194.1; 15, 174.1; 16.5, 156.1; 18, 139.2.

months. The degree of stability and reproducibility obtained in these experiments is about the same as reported in many earlier investigations of this type, but is far better than found by Deneux *et al.*

The measurements on the Fe^{2+} malonate system have been made with great variations of the ratio $C_{\text{H}}/C_{\text{A}}$ and of C_{M} in the solutions, so that the formation of protonated or polynuclear species could be detected. Some of the measurements were made in poorly buffered solutions at such high pH values that possibly present Fe^{3+} should be strongly hydrolyzed or bound to malonate ion, thus causing a considerable error in the determination of the concentration of free ligand ion from the emf readings. To prevent that any oxidation from the ferrous to the ferric state occurred during the measurements, all solutions were swept free from dissolved oxygen prior to use. The measured emf values have been corrected for liquid junction potentials as described earlier.⁷

The measurements on the Fe^{3+} malonate system has been made in the following way. The titrand contains Fe^{3+} and perchloric acid and the titrant was a malonate buffer. In a series of titrations, the concentration free hydrogen ion, h , has been kept approximately constant, $h \approx 50 \text{ mM}$, while C_{M} has been varied. The measurements have then been performed

at another constant h -value, $h \approx 150 \text{ mM}$. One series (number 3 in Table 1) has been performed at lower h -values. Table 1 contains some of the experimental data, the complete data can be obtained from the author.

For the Fe^{3+} oxalate system, the preliminary results showed a fair agreement with the results of Deneux *et al.* and a detailed investigation was considered unnecessary. Two titrations were made and gave 36 experimental points. To retard the photochemical decomposition of Fe(III) in oxalate solutions, the solutions were kept in dark during the measurements.

The calorimetric measurements were performed as titrations. Two types of titrations were made: either a ferric ion solution was titrated with an oxalate (malonate) buffer, or the buffer solution was titrated with the metal ion solution. In this way solutions with \bar{n} values up to 2.8 (for the oxalate system) or up to 2.2 (for the malonate system) have been investigated. Other details of the procedure have been described earlier.^{12,13}

CALCULATIONS AND RESULTS

Potentiometric measurements

i. The Fe^{2+} malonate system. The stability constants for this system have been calculated from the experimentally determined values of v/ml and E/mV by the least squares procedure "Letagrop Vrid",¹⁴ and also by standard graphical procedures. The data were described by assuming the existence of two Fe^{2+} malonate complexes, FeA and FeA_2^{2-} , with the following stability constants:

$$\beta_{101} = (1.49 \pm 0.05) \times 10^3 \text{ M}^{-1}$$

$$\beta_{102} = (1.62 \pm 0.20) \times 10^3 \text{ M}^{-2}$$

(The errors here and in the following are equal to 3σ , where σ denotes the standard deviation). 111 experimental points were included in the calculation, and the standard deviation in the error carrying variable $C_{\text{H}}/C_{\text{A}}$ was equal to 3.8×10^{-3} , which indicates that the experimental values are quite satisfactorily described by the calculated constants. Some experimental and calculated \bar{n} vs. $-\lg(a/\text{M})$ values are shown in Fig. 1.

The assumption that an acid complex with the composition FeHA^+ is formed does not improve the fit between experimental and calculated values, and the corresponding stability constant β_{111} is not significantly positive. It is possible to give an estimate of the max-

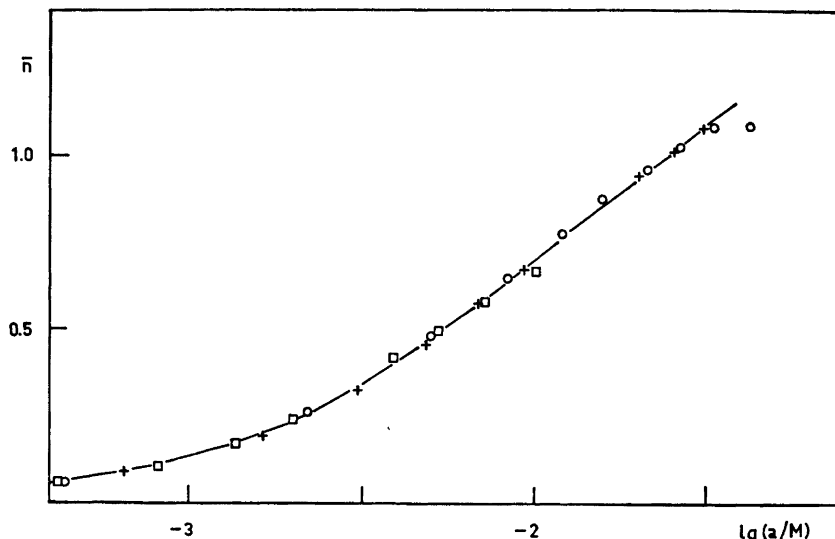


Fig. 1. Experimental \bar{n} vs. $-\lg(a/M)$ data for the Fe^{2+} malonate system. The curve has been calculated with the stability constants given in the text.

Symbol	Solution S C_H/mM	C_M/mM	C_A/mM	Solution T C_H/mM	C_M/mM	C_A/mM
○	16.2	14.2	0	114	0	255
+	32.4	28.4	0	114	0	255
□	16.2	14.2	0	147	0	198

imum value of β_{111} , and both the least squares calculations and graphical evaluations indicate that β_{111} is less than $2 \times 10^5 \text{ M}^{-2}$. There is no indication of the formation of polynuclear species.

ii. *The Fe^{3+} oxalate system.* As the available "Letagrop" program is not adopted for this type of four component systems, a computer program that calculated E/mV values from values of total concentrations and stability constants was written. The stability constants were varied until the best fit between calculated and observed E/mV values was obtained, that is, the error square sum $\sum(E_{\text{calc}} - E_{\text{obs}})^2$ was minimized, where the summation is over all experimental values.

Although the measurements have been designed so that the hydrolysis of ferric ion should be small in the solutions studied, the formation of FeOH^{2+} and $\text{Fe}_2(\text{OH})_2^{4+}$ has been accounted for by using the hydrolysis constants

$$\beta_{1-10} = 1.5 \times 10^{-3} \text{ M}$$

$$\beta_{2-20} = 1.9 \times 10^{-3} \text{ M}^2$$

The value for β_{1-10} is an average of several values quoted in Stability Constants,¹ and β_{2-20} is from Milburn, as cited by Sillén.¹ The stability constants for the Fe^{2+} oxalate system must be known; the values of Bottari and Ciavatta have been used.⁹

The following stability constants for the proton oxalate complexes in 1 M NaClO_4 were taken from Moorhead and Sutin:⁴

$$\beta_{011} = 3.58 \times 10^3 \text{ M}^{-1}$$

$$\beta_{021} = 4.27 \times 10^4 \text{ M}^{-2}$$

The calculations on 36 experimental points from two titration series gave the following stability constants for the formation of the Fe^{3+} oxalate complexes:

$$\beta_{101} = (3.83 \pm 0.15) \times 10^7 \text{ M}^{-1};$$

$$\lg(\beta_{101}/\text{M}^{-1}) = 7.58$$

$$\beta_{102} = (6.4 \pm 0.3) \times 10^{13} \text{ M}^{-2};$$

$$\lg(\beta_{102}/\text{M}^{-2}) = 13.81$$

$$\beta_{103} = (4.6 \pm 0.6) \times 10^{18} \text{ M}^{-3};$$

$$\lg(\beta_{103}/\text{M}^{-3}) = 18.66$$

The standard deviation in the emf E was 0.2 mV.

iii. The Fe³⁺ malonate system. Table 1 gives some of the experimental data for this system. The calculations on this system were performed in the same way as for the oxalates. (The stability constants for the proton malonate complexes were taken from Ref. 7). It is also possible to use a graphical method, due to Fronæus,¹⁵ on each set of titrations at a (nearly) constant value of the concentration free hydrogen ion, h , but at various C_M values. The value of β_{101} obtained in this way was in precise agreement with the value obtained from the numerical procedure. The value of β_{101} was calculated from each titration series. Each set of measurements at constant h but at various C_M values could be described with one value of β_{101} , which indicates that the formation of polynuclear species is negligible in the concentration range studied. If an acid complex is formed, *e.g.* FeHA²⁺, one expects the calculated stability constant, β^*_{101} , to vary linearly with h :

$$\beta^*_{101} = \beta_{101} + h\beta_{111} \quad (1)$$

The value obtained, $\beta^*_{101} = (3.14 \pm 0.04) \times 10^7 \text{ M}^{-1}$, describes the measurements, in which h varied from about 40 mM to 150 mM, and no systematic variation of β^*_{101} with h was observed. If eqn. (1) is applied, an "extreme" interpretation of the findings is that $\beta_{101} = 3.08 \times 10^7 \text{ M}^{-1}$ and $\beta_{111} = 7 \times 10^6 \text{ M}^{-2}$. This value of β_{111} thus represents the upper limit of β_{111} that is reconcilable with the experimental data, but the data are best described by the following three stability constants:

$$\beta_{101} = (3.14 \pm 0.04) \times 10^7 \text{ M}^{-1};$$

$$\lg(\beta_{101}/\text{M}^{-1}) = 7.50$$

$$\beta_{102} = (1.09 \pm 0.06) \times 10^{13} \text{ M}^{-2};$$

$$\lg(\beta_{102}/\text{M}^{-2}) = 13.04$$

$$\beta_{103} = (4 \pm 2) \times 10^{18} \text{ M}^{-3};$$

$$\lg(\beta_{103}/\text{M}^{-3}) = 16.6$$

The values are based on in all 16 series with 356 experimental points. The standard
Acta Chem. Scand. A 31 (1977) No. 6

deviation in the emf E was 0.15 mV.

The error in β_{103} is considerable, due to the lower reproducibility of the measured emf values in solutions with high \bar{n} values, and also because the highest \bar{n} value obtained is only 2.1.

Schaap *et al.* have polarographically obtained a value for the ratio of the dissociation constants of the tris(malonato)ferrate(III) ion and the bis(malonato)ferrate(II) ion.¹⁶ Combining this number with the stability constant for the bis(malonato)ferrate(II) ion obtained in this work leads to $\beta_{103} = (5.1 \pm 1.3) \times 10^{18} \text{ M}^{-3}$ for the formation of Fe[CH₂(COO)₂]₃³⁻.

Calorimetric measurements

All enthalpy values have been calculated with the least squares program "Letagrop Kalle" from the experimental (v/ml , Q/J) values. The overall enthalpies of protonation of malonate ion at 25 °C in 1 M NaClO₄ are known,¹³ while the corresponding values for the oxalate system were determined. From 11 experimental points, the following values were calculated:

$$\Delta H^\circ_{011} = (4.0 \pm 0.2) \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{021} = (5.2 \pm 0.9) \text{ kJ mol}^{-1}$$

The enthalpy of hydrolysis of Fe³⁺ in 1 M NaClO₄ has not been determined, but Arnek has calculated $\Delta H^\circ_{1-10} = (46.0 \pm 7.5) \text{ kJ mol}^{-1}$ and $\Delta H^\circ_{2-20} = 41.8 \text{ kJ mol}^{-1}$ from Schlyter's measurements in 3 M NaClO₄.¹⁷ Some ΔH°_{1-10} values within the limits given by Arnek were tried and the best fit was obtained with $\Delta H^\circ_{1-10} = 38 \text{ kJ mol}^{-1}$. The formation of Fe₂(OH)₂⁴⁺ is small in the solutions used and no variation of ΔH°_{2-20} was tried. The calculated overall enthalpy values are listed in Table 2, together with ΔH° and ΔS° values.

The obtained values for the standard deviation in Q are of the same magnitude as obtained earlier with this type of equipment.¹³ The error in the enthalpy of formation of Fe(mal)₃³⁻ is especially great, mainly due to the fact that the maximum \bar{n} value in the solutions used is as low as 2.2.

DISCUSSION

A direct comparison of the stability constants obtained here for the Fe²⁺ malonate

Table 2. The overall enthalpy, Gibbs energy, and entropy changes for the formation of Fe³⁺ oxalate and malonate complexes. The number of experimental points and the standard deviation in the Q values in the calorimetric measurements are given. The uncertainties are equal to three times the standard deviations.

Reaction	Number of experimental points	Standard deviation in Q/J	ΔH° kJ mol ⁻¹	$-\Delta G^\circ$ kJ mol ⁻¹	ΔS° J K ⁻¹ mol ⁻¹
Fe ³⁺ + ox ²⁻ → Fe ox ⁺	17	0.09	6.3 ± 0.9	43.28 ± 0.10	166 ± 3
Fe ³⁺ + 2ox ²⁻ → Fe ox ₂ ⁻			3.7 ± 1.8	78.80 ± 0.12	277 ± 6
Fe ³⁺ + 3ox ²⁻ → Fe ox ₃ ³⁻			0.4 ± 1.3	106.5 ± 0.3	359 ± 4
Fe ³⁺ + mal ²⁻ → Fe mal ⁺	20	0.05	11.3 ± 0.2	42.79 ± 0.03	181.4 ± 0.7
Fe ³⁺ + 2mal ²⁻ → Fe mal ₂ ⁻			14.4 ± 0.7	74.41 ± 0.14	298 ± 2
Fe ³⁺ + 3mal ²⁻ → Fe mal ₃ ³⁻			9.8 ± 7.3	94.8 ± 1.7	351 ± 25

complexes with the data of Nancollas *et al.*^{18,19} is not possible, as their data refer to a very low ionic strength. However, the first Fe³⁺ oxalate complex is 5.0 kJ/mol more stable than the malonate complex, which value is intermediate between the corresponding values for the Mn²⁺ and Co²⁺ complexes. The result also conforms to the general observation that oxalate complexes are more stable than the corresponding malonates.

Hydrogen malonate ion complexing has been observed with the trivalent lanthanoid ions,⁷

but not with the divalent transition metal ions. The lanthanoid-hydrogen malonate complexes are somewhat less stable than the corresponding acetate complexes. The upper limit for β_{111} found here corresponds to an equilibrium constant for the equilibrium between Fe³⁺ ion and hydrogen malonate ion of less than 1.8 M⁻¹. The β_1 value for the Fe³⁺ acetate complex is 2.1 M⁻¹ (at 20 °C).²⁰

The stability constants of the ferric ion oxalate and malonate complexes are collected in Table 3, together with some literature values.

Table 3. Some values of stability constants of iron(III) with oxalate, malonate and succinate ion at 25 °C.

lg (β_{101}/M^{-1})	lg (β_{102}/M^{-2})	lg (β_{103}/M^{-3})	Ionic strength	Ref.
Oxalate				
7.58	13.81	18.66	1 M NaClO ₄	This work
7.54	14.59	20.0	0.5 M NaNO ₃ ^a	6
7.59	—	—	1 M NaClO ₄	4
7.53	13.64	18.49	0.5 M LiClO ₄	2
7.56	—	—	1 M NaClO ₄	5
—	—	18.54 ^b	~1 M NaClO ₄	16
Malonate				
7.50	13.04	16.6	1 M NaClO ₄	This work
7.46	—	—	0.5 M LiClO ₄	2
—	—	16.7 ^c	~1 M NaClO ₄	16
6.54, lg(β_{111}/M^{-2}) = 7.59	—	—	1 M NaClO ₄	5
Succinate				
6.52	—	—	1 M NaClO ₄ ^a	22
6.88	—	—	0.5 M LiClO ₄	2

^a Temperature not given. ^b Calculated with auxiliary data from Ref. 9. ^c Calculated with auxiliary data from this paper.

The agreement is good, with one exception: the results of Gordienko *et al.* on the Fe^{2+} malonate system. It should be noted that Gordienko's acidity constants for malonic acid differ considerably from the results of two other investigations.^{7,21} It also seems unlikely that protonated complexes, as FeHA^{2+} , should be formed in the malonate system but not in the succinate system.²² It thus seems probable that Gordienko's measurements on the malonate system are beset with some systematic error.

The lanthanoid acetate complexes are about 1–2 kJ mol⁻¹ more stable than the corresponding hydrogen malonate complexes. This difference is much greater, at least 7 kJ mol⁻¹, for the corresponding ferric ion complexes.

It has also been shown that the strength of the acid MHA^{2+} steadily increases as the radius of the lanthanoid ion M^{3+} decreases. This behaviour has been described in simple electrostatic terms.⁷ The upper limit of β_{111} for FeHA^{2+} determined here shows that FeHA^{2+} is a much stronger acid than the lanthanoid hydrogen malonates, in keeping with the smaller size of the iron(III) ion. It is suggested that this finding indicates that the malonate ion has a very strong tendency to form a chelate complex with ferric ion. It is noteworthy that the ferric monooxalate complex is only 0.5 kJ mol⁻¹ more stable than the malonate complex. The trivalent rare earth oxalate complexes are about 7 kJ/mol more stable than the malonates.

The ratios of the stepwise stability constants are different for the oxalates and malonates: K_1/K_2 and K_2/K_3 are equal to 23 for the oxalates and 92 for the malonates. This increased difficulty for the formation of the higher malonate complexes as compared to the oxalates might be caused by different geometrical requirements of the bulkier malonate ion. Structural data would be of interest for a more detailed discussion, but only the structure of $\text{K}_3[\text{Fe ox}_3] \cdot 3\text{H}_2\text{O}$ is known at present.²³

It can be seen from Table 2 that the stepwise enthalpy changes become less positive for the higher complexes. The ferric ion malonate complexes are similar to the rare earth malonates in this respect. The complexes are stabilized by the large positive entropy changes, due to the liberation of water molecules from the metal ion. The stepwise entropy changes

become less positive for the higher complexes, which can be described as caused by the coordinated water molecules being less firmly bound in a higher complex than in a lower.

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