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Determination of the Constants of Formation of Complexes of Iron(III) and Acetohydroxamic Acid

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1. Introduction

Simple hydroxamic acids (XHA) are hydrophilic organic compounds with the general formula RCONHOH that can act as O,O donor ligands with high affinities for hard cations such as Fe^{3+}, Np^{4+} and Pu^{4+} with which they form 5-membered chelate rings (Muri et al.,2002; Desaraju & Winston,1986; Carrott et al.,2007).

They have a wide range of applications in many fields, including as enzyme inhibitors, soil enhancers, fungicides, mutagens, carcinogens, DNA cleavers, drug delivery systems (Ghosh,1997), ion exchange (Vernon,1982) and materials research (Ghosh,1997). Siderophores such as the desferrioxamines contain multiple hydroxamate functionalities and are naturally occurring ligands specifically used by fungi for the sequestration of iron from the environment (Raymond et al.,1984; Renshaw et al.,2002; Monzyk & Crumbliss,1979). The potential role of such hydroxamate siderophores in the mobilisation of actinide ions within the environment has also been considered (John et al.,2001).

More recently, XHAs have also been identified as useful reagents for the control of Pu and Np in advanced PUREX and UREX processes proposed for the processing of spent nuclear fuel (Birkett et al.,2005). In such separation processes, U, Np and Pu are separated according to oxidation state specific aqueous/non aqueous solvent extraction in the presence of acetohydroxamic acid (AHA) (Carrott et al.,2007). In this context, Fe(III) is a useful non-radioactive analogue for the interrogation of the complexation behaviour of actinides.
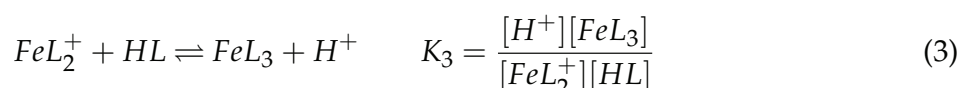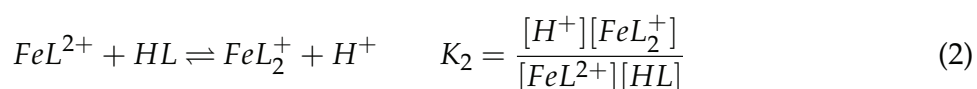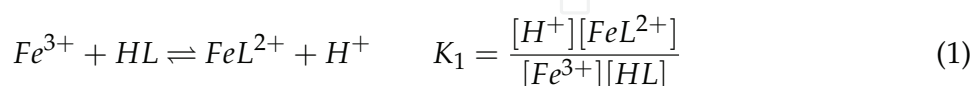
It is also well known that hydroxamic acids are susceptible to hydrolysis, particularly in acidic solutions (Ghosh,1997). Whilst there have been many studies of hydroxamic acid hydrolysis and their complexation reactions with metal ions, there have been relatively few studies of the stability of the metal-hydroxamate complexes towards hydrolysis. We have previously reported on the kinetics of the hydrolysis of hydroxamic acids both in free solution and when bound to metal ions and developed a kinetic model describing this process at room temperature (Andrieux et al.,2007; Andrieux et al.,2008; Carrott et al.,2008). However, the applications of hydroxamic acids in biological-related fields requires an understanding of the behaviour of these systems at temperatures of biological interest, for example in vivo (310K) or temperatures at which proteins start to denature ($\sim$ 325K) (Roos,2006). Additionally, the temperature dependencies of the equilibrium constants are useful in gaining a better understanding of the complexation processes and the role of enthalpy and entropy in complex formation. As a precursor to any temperature-dependent kinetic study of Fe(III)-AHA

hydrolysis, comprehensive and reliable thermodynamic data are required on the Fe(III)-AHA complexation reactions, which is the focus of this study.

Furthermore, we are applying the kinetic models developed for the Fe(III)-AHA system to the kinetics of the hydrolysis of hydroxamic acids when bound to actinide ions such as Pu^{4+} and Np^{4+} in support of advanced PUREX and UREX processes (Andrieux et al.,2008).

Thus, a study of the temperature dependence of the speciation of the Fe^{3+}-AHA system will both provide a useful addition to the thermodynamic database of Fe(III) in its own right and support advanced PUREX/UREX process development through its role as a non-active analogue of e.g. the Np^{4+}-AHA system.

As mentioned above, hydroxamic acids readily form stable complexes with Fe^{3+} ions according to reactions described in eqs. (1)-(3):

$$Fe^{3+} + HL \rightleftharpoons FeL^{2+} + H^+ \qquad K_1 = \frac{[H^+][FeL^{2+}]}{[Fe^{3+}][HL]} \qquad (1)$$

$$FeL^{2+} + HL \rightleftharpoons FeL_2^+ + H^+ \qquad K_2 = \frac{[H^+][FeL_2^+]}{[FeL^{2+}][HL]} \qquad (2)$$

$$FeL_2^+ + HL \rightleftharpoons FeL_3 + H^+ \qquad K_3 = \frac{[H^+][FeL_3]}{[FeL_2^+][HL]} \qquad (3)$$

where L represents the deprotonated acetohydroxamato ligand and all equilibrium constants are calculated from concentrations rather than activities.

Values of the equilibrium constant for the formation of the monoacetohydroxamatoiron(III) complex were reported in the literature with Monzyk et al. suggesting K_1 = 109 (Monzyk & Crumbliss,1979) without specifying an equilibrium temperature, while Schwarzenbach et al. report a value for the log K_1 = 2.28 at 293 K (Schwarzenbach & Schwarzenbach,1963), corresponding to K_1 = 190.5. The inconsistency of these values together with a lack of data pertaining to their temperature dependence has prompted us to conduct our own determination of values for K_1, K_2 and K_3. This, we have done through measurement of the electronic absorption spectra of a range of mixtures of the three Fe(III)-AHA complexes and the development of a simple analytical method for the extraction of values of equilibrium constants from those spectra. We have also deployed this method for the measurement of the temperature dependence of these equilibrium constants prior to the construction of useful temperature-dependent speciation diagrams.

2. Materials and methods

2.1 Materials

All reagents, including HNO_3 (70%, AnalaR, BDH Chemicals Ltd., Poole, Dorset, UK) and AHA (Sigma-Aldrich Ltd, UK) were obtained from reputable suppliers (Aldrich, Fluka) at the highest available purity and used as received. AHA was stored in a conventional refrigerator at 4°C in order to prevent its decomposition. Solutions were prepared using doubly distilled water, produced by a home-made still and further purified by a deionisation system (E pure model 04642, Barnstead/Thermodyne, Dubuque, Iowa, USA) to a resistivity of 1.8×10^5 Ω m.

2.2 Methods

UV-visible absorbance spectra of complex and complex-precursor solutions were measured by spectrophotometry (Diode Array model 8452A, Hewlett Packard, USA) fitted with a

HP89090A Peltier temperature controller. Solutions for spectroscopic measurement were prepared from stock (Fe(III)) or freshly made solutions (AHA, prepared immediately prior to experiment) and pipetted into an optical cuvette (pathlength 1 cm). The complexant (AHA) was added last. The volume of complexant required was always small and had no effect on the temperature of the receiving solution when added. The spectra were then measured as soon as possible after mixing. All experiments were performed at pH < 1 in order to minimise hydrolysis of free ferric ions and the formation of iron hydroxides and oxyhydroxides, as discussed in the following section.

3. Results and discussion

3.1 Iron hydrolysis

It is well known that Fe^{3+} readily hydrolyses in water in accordance with:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \tag{4}$$

the first step in a series of deprotonation / polymerisation reactions that ultimately result in the formation of ferric hydroxides and oxyhydroxides. Using the most recently published, critically assessed Gibbs energies of formation of the various species involved (Cornell & Schwertmann,1996; Heusler & Lorenz,1985), the equilibrium constant for this first deprotonation can be calculated as being equal to 6.78 x 10^{-3} at 298 K, corresponding to a pK_a(Fe^{3+} / $FeOH^{2+}$) of 2.17.

Figure 1 shows the speciation of the two iron-containing species of equation (4) as a function of pH, calculated at T=298K for a total iron(III) concentration of 0.5 mol dm^{-3} and an ionic strength of 0.1 mol dm^{-3}. From this, it may be seen that $FeOH^{2+}$ will become the dominant species above pH=2.17, but that it will also be present in significant amounts at lower pH values. In fact, 10% of all iron(III) is present as the hydroxide at pH values as low as 1.2. In order to facilitate subsequent calculations, it is therefore advisable to carry out spectroscopic measurements at pH values up to 1 (where no more than 6.3% of all iron(III) is present as the hydroxide).
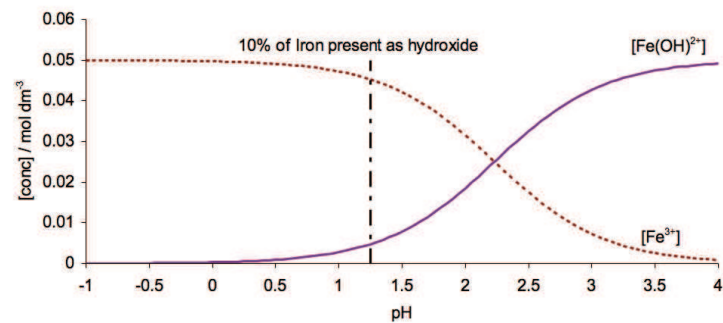

Fig. 1. Speciation diagram for Fe^{3+} and $FeOH^{2+}$ as a function of pH for a total iron(III) concentration of 50×10^{-3} mol dm^{-3} calculated at an ionic strength of 0.1 mol dm^{-3}

The equilibrium constant for the reaction shown in Eq. 4 has been studied as a function of temperature (T = 298-353 K) and ionic strength (I = 0.1-2.67 mol dm^{-3}) in perchlorate media by Sapieszko et al. (Sapieszko et al.,1977). Using their data, we have calculated that, in order to prevent significant formation of hydrolysed iron(III) under the conditions of our experiments (T = 293-323 K, and I ~ 0.1 mol dm^{-3}), the value of the pH to be used in the determination

of the equilibrium constants of formation of the acetohydroxamatoiron(III) complexes should not exceed 1 at T > 300 K. Any data presented at pH > 1 at T > 300 K is shown for the purposes of context only.

3.2 General methodology

The general approach used in the determination of the thermodynamic constants of formation of the various iron(III)-AHA complexes may be described by the following. In a solution containing any amount of iron(III) and acetohydroxamic acid, the concentrations of the various species in solution as a result of the establishment of the equilibria described in equation (1) to (3) may be expressed as follows:

$$[FeL^{2+}] = \xi_1 \tag{5}$$

$$[FeL_2^+] = \xi_2 \tag{6}$$

$$[FeL_3] = \xi_3 \tag{7}$$

$$[Fe^{3+}] = [Fe^{3+}]_i - \xi_1 - \xi_2 - \xi_3 \tag{8}$$

$$[HL] = [HL]_i - \xi_1 - 2\xi_2 - 3\xi_3 \tag{9}$$

$$[H^+] = [H^+]_i + \xi_1 + 2\xi_2 + 3\xi_3 \tag{10}$$

where $[Fe^{3+}]_i$, $[HL]_i$ and $[H^+]_i$ represent the initial concentration of iron(III), acetohydroxamic acid and nitric acid, respectively.

These may then be used to express the equilibrium constants for the formation of the various complexes in terms of ξ_1, ξ_2 and ξ_3 as the only unknown parameters, and the resulting equations may be solved as simple polynomial expressions. The following section describes the hypotheses made and the specific methodology used in the determination of the equilibrium constant of formation of the monoacetohydroxamatoiron (III) complex.

3.3 Thermodynamics of monoacetohydroxamatoiron (III) complex formation

The determination of K_1 is best carried out under conditions where the monoacetohydroxamatoiron(III) complex is present in a vast excess compared to both the bis- and trisacetohydroxamatoiron(III) complexes, i.e. in the presence of a very large excess of iron compared to the hydroxamate. Under such conditions, equation (1) may be expressed in terms of the parameters defined in equations (5)-(10) as:

$$K_1 = \frac{\xi_1([H^+]_i + \xi_1)}{([Fe^{3+}]_i - \xi_1)([HL]_i - \xi_1)} \tag{11}$$

which contains two unknown parameters K_1 and ξ_1. In order to solve equation (11) it is then necessary to use two data sets for each temperature considered. This may be achieved by varying the pH of the solution, thereby altering the concentration of the complex. It is then possible, from the spectroscopic data to express the complex concentration of one of the samples as a function of the complex concentration of the other, *via*:

$$\frac{\xi_{1_1}}{\xi_{1_2}} = \frac{Abs_1}{Abs_2} = x \tag{12}$$

where the very last digit of the subscript in each term refers to the arbitrarily assigned experiment number and x is the ratio of the absorbance due to the mono-complex in each of the samples considered. For each of the two experiments, equation (11) may then be re-written as:

$$K_1 = \frac{\xi_{1_1}([H^+]_{i_1} + \xi_{1_1})}{([Fe^{3+}]_{i_1} - \xi_{1_1})([HL]_{i_1} - \xi_{1_1})} \qquad \text{for experiment 1} \tag{13}$$

and

$$K_1 = \frac{x\xi_{1_1}([H^+]_{i_2} + x\xi_{1_1})}{([Fe^{3+}]_{i_2} - x\xi_{1_1})([HL]_{i_2} - x\xi_{1_1})} \qquad \text{for experiment 2} \tag{14}$$

These two equations may then be equated and re-arranged to give the polynomial expression of the second order shown in equation (15).

$$\xi_{1_1}([H^+]_{i_1} + \xi_{1_1})([Fe^{3+}]_{i_2} - x\xi_{1_1})([HL]_{i_2} - x\xi_{1_1}) -$$
$$x\xi_{1_1}([H^+]_{i_2} + x\xi_{1_1})([Fe^{3+}]_{i_1} - \xi_{1_1})([HL]_{i_1} - \xi_{1_1}) = 0 \tag{15}$$

Solution of equation (15) yields a value of ξ_{1_1} and enables the calculation of K_1. Three data sets are sufficient to calculate three values of K_1 allowing for an average to be taken. Figure 2 shows the UV-visible spectra recorded from three solutions at different pH values at 313K. From that, it may be seen that the λ_{max} value is independent of pH.
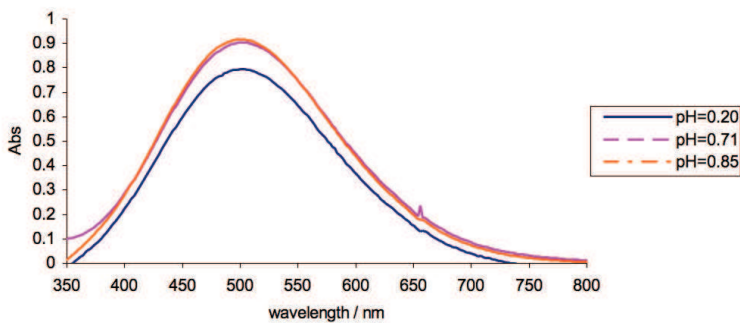

Fig. 2. Typical UV-visible spectra of a solution containing the monoacetohydroxamatoiron (III) complex (initial solution composition: [Fe^{3+} = 50x10^{-3} mol dm^{-3}, [HL] = 10^{-3} mol dm^{-3}) recoded at T = 313K and pH = 0.20, 0.71 and 0.85 respectively. λ_{max} = 510nm.

Table 1 shows the absorbance of three solutions containing the monoacetohydroxamatoiron (III) complex at three different pH values at the range of temperature considered, together with the calculated average and standard deviation values of K_1 as a function of temperature. One notation of the Van't Hoff isochore, equation (16), predicts that Ln(K_1) should be linearly dependent on T^{-1}. Figure 3 shows such a plot for the data of Table 1.

$$Ln(K) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{16}$$

T/K	Abs @ 510nm, pH = 0.20	Abs @ 510nm, pH = 0.71	Abs @ 510nm, pH=0.85	Average K_1	Standard deviation
293	0.803	0.921	0.912	65.25	0.68
298	0.793	0.916	0.902	40.65	5.79
303	0.793	0.912	0.889	28.22	11.4
313	0.779	0.894	0.877	14.58	4.17
323	0.667	0.858	0.842	4.24	0.54

Table 1. Determination of K_1 in accordance with equation (15) as a function of temperature, calculated from solutions with $[Fe^{3+}]_i = 50 \times 10^{-3}$ mol dm^{-3} and $[HL]_i = 10^{-3}$ mol dm^{-3}

where R is the universal gas constant and ΔH^o and ΔS^o are the standard enthalpy and standard entropy of reaction, respectively, assumed to be constant over the temperature range of our experiments.
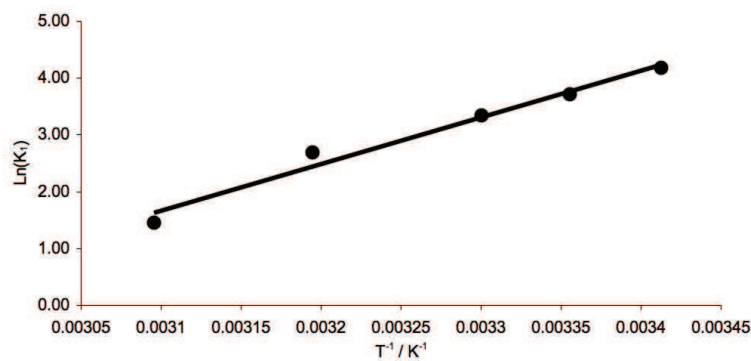

Fig. 3. Ln(K_1) vs. T^{-1} for the formation of the monoacetohydroxamatoiron(III) complex. Regression line : $Ln(K_1) = 8253 T^{-1} - 23.934; R^2 = 0.9783$

The good linearity of the plot in figure 3 supports our earlier assumption that ΔH^o and ΔS^o are invariant with regards to temperature in the range 293-323K.
From the regression line of figure 3, and according to equation (16), the standard enthalpy of reaction is found to be -68.6 kJ mol^{-1} and the standard entropy of reaction is found to be -199.0 J mol^{-1} K^{-1}. The negative value of ΔH^o indicates that the complexation process is exothermic in nature, while the negative value of ΔS^o suggests that the process is accompanied by a loss of entropy and is therefore enthalpically driven.

3.3.1 Extinction coefficient determination

In addition to having determined a reliable value of K_1 over the range of temperature considered, the determination of the various concentrations of the monoacetohydroxamatoiron(III) complex at a range of pH values and temperatures affords the possibility of calculating the extinction coefficient of the former, ϵ_1, by use of Beer's Law:

$$A = \epsilon l \zeta_1 \tag{17}$$

where A is the absorbance of the sample at the wavelength of interest (here λ_{max} = 510nm) and l the pathlength of the cell (1 cm). The extinction coefficient of the monoacetohydroxamatoiron(III) complex is then found to be $\epsilon_1 = 1005 \pm 13$ dm^3 mol^{-1} cm^{-1},

with all calculated values being within 1.5% of the calculated average, an acceptable level of experimental error.

3.4 Thermodynamics of bisacetohydroxamatoiron (III) complex formation

The determination of the value of K_2 necessitates the preparation of solutions where the bisacetohydroxamatoiron(III) complex (FeL_2^+) is in equilibrium with either the monoacetohydroxamatoiron(III) or the trisacetohydroxamatoiron(III) (FeL_3) complex. This presents an additional difficulty compared to the determination of K_1 as it is not possible to consider both ξ_1 and ξ_3 to be negligible compared to ξ_2. However, knowledge of the individual absorption spectra and the extinction coefficient of the monoacetohydroxamatoiron(III) complex provide us with a simple means of deconvoluting spectrometric data relating to solutions containing a mixture of the mono- and bis- complexes and alleviating this issue. The description of the method used forms the basis of the next section.

3.4.1 Deconvolution of spectrometric data

The spectrum of a solution containing a mixture may be deconvoluted *via* the exploitation of the law of additivity of absorbance, which states that as long as two or more species do not interact chemically with one another the absorbance of the mixture (A_T) is equal to the sum of the absorbances of each individual species, according to:

$$A_T = \sum_i A_i = \sum_i \epsilon_i\, c_i\, l \tag{18}$$

where c is the concentration of each individual species i. Using this principle, the spectrum of the FeL_2^+ may be obtained by subtracting the spectrum of FeL^{2+}, multiplied by a scaling factor, from the measured spectrum of the mixture. The scaling factor is adjusted until the λ_{max} of the deconvoluted spectrum of the bisacetohydroxamatoiron(III) complex matches the literature values of 470nm (Desaraju & Winston,1986). This technique assumes that the concentration of FeL_3 is negligible compared to that of the two other complexes. Figure 4 shows the typical deconvolution of a spectrum recorded for a solution containing 5×10^{-4} mol dm^{-3} iron(III) and 0.2 mol dm^{-3} HL at pH=0.61, T=298K.
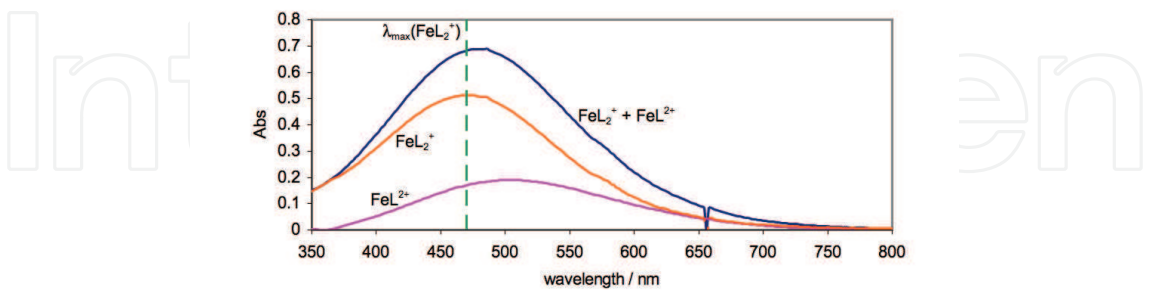

Fig. 4. Typical deconvolution of a spectrum recorded for a solution containing 5×10^{-4} mol dm^{-3} iron(III) and 0.2 mol dm^{-3} HL at pH=0.61, T=298K

3.4.2 Determination of K$_2$

The formation of the bisacetohydroxamatoiron(III) complex may be envisaged as either the stepwise formation of FeL^{2+} followed by the formation of FeL_2^+ or the simultaneous formation of a mixture of both complexes, the latter resulting in the definition of a new equilibrium constant for the formation of the bisacetohydroxamatoiron(III) complex from acetohydroxamic acid and iron(III), K_2'. Although this leads to a more complex mathematical expression, it is the preferred option in the determination of ξ_2 as it explicitly takes into account the presence of free iron(III) as well as that of the monoacetohydroxamatoiron(III) complex .

$$K_2' = K_1 K_2 = \frac{[FeL_2^+][H^+]^2}{[Fe^{3+}][HL]^2} \tag{19}$$

equation (19) may be expressed in terms of the parameters defined in equations (5)-(10), under conditions where ξ_3 is negligible as:

$$K_2' = \frac{\xi_2 \left([H^+]_i + \xi_1 + 2\xi_2\right)^2}{\left([Fe^{3+}]_i - \xi_1 - \xi_2\right) \left([HL]_i - \xi_1 - 2\xi_2\right)^2} \tag{20}$$

Using the extinction coefficient for the monoacetohydroxamatoiron(III) complex and the deconvoluted spectra for the mixture of mono- and bisacetohydroxamatoiron(III), it is possible to extract values of ξ_1 for all data recorded, leaving equation (20) with only two unknown parameters (K_2' and ξ_2). Using an approach similar to that used in the determination of K_1, it is possible to use the spectra recorded for two samples at the same temperature but different pH values to extract values of ξ_2 and enable the determination of K_2. Here the ratio of concentration is defined as y:

$$\frac{\xi_{2_1}}{\xi_{2_2}} = \frac{Abs_1}{Abs_2} = y \tag{21}$$

where the very last digit of the subscript in each term refers to the arbitrarily attributed experiment number. This results in the establishment of the soluble system of two equations with two unknowns:

$$K_2' = \frac{\xi_{2_1} \left([H^+]_{i_1} + \xi_{1_1} + 2\xi_{2_1}\right)^2}{\left([Fe^{3+}]_{i_1} - \xi_{1_1} - \xi_{2_1}\right) \left([HL]_{i_1} - \xi_{1_1} - 2\xi_{2_1}\right)^2} \tag{22}$$

$$K_2' = \frac{y\xi_{2_1} \left([H^+]_{i_2} + \xi_{1_2} + 2y\xi_{2_1}\right)^2}{\left([Fe^{3+}]_{i_2} - \xi_{1_2} - y\xi_{2_1}\right) \left([HL]_{i_2} - \xi_{1_2} - 2y\xi_{2_1}\right)^2} \tag{23}$$

which may be equated and re-arranged to yield the 6th order polynomial expression:

$$\xi_{2_1} \left([H^+]_{i_1} + \xi_{1_1} + 2\xi_{2_1}\right)^2 \left([Fe^{3+}]_{i_2} - \xi_{1_2} - y\xi_{2_1}\right) \left([HL]_{i_2} - \xi_{1_2} - 2y\xi_{2_1}\right)^2 -$$

$$y\xi_{2_1} \left([H^+]_{i_2} + \xi_{1_2} + 2y\xi_{2_1}\right)^2 \left([Fe^{3+}]_{i_1} - \xi_{1_1} - \xi_{2_2}\right) \left([HL]_{i_1} - \xi_{1_1} - 2\xi_{2_1}\right)^2 = 0 \tag{24}$$

Equation (24) may not be trivially solved analytically but may be solved by a straightforward computation. A spreadsheet calculating the result of the lefthand side of equation (24) as a function of ξ_{2_1} is generated and the roots are inspected to identify the single root

corresponding to a meaningful value for the concentration of FeL_2^+ (i.e. $0 < \xi_{2_1} \leq [Fe^{3+}]_{i_1}$). This value is then used to calculate the equilibrium concentrations of all other species in solution according to equations (5)-(10) enabling the determination of K_2 according to equation (2). Three data sets allow for three values of K_2 to be calculated and an average to be taken. Table 2 shows the values of the absorbance of the mono- and bisacetohydroxamatoiron(III) complex from the deconvoluted data, together with the calculated average and standard deviation values of K_2.

T/K	Abs_{mono} @ 510nm			Abs_{bis} @ 470nm			Average K_2	Standard Deviation
	pH=0.40	pH=0.61	pH=0.74	pH=0.40	pH=0.61	pH=0.74		
293	0.419	0.199	0.080	0.338	0.505	0.696	2.638	2.055
298	0.449	0.190	0.085	0.317	0.512	0.691	2.561	1.934
303	0.449	0.199	0.090	0.314	0.502	0.686	2.340	1.782
313	0.469	0.239	0.120	0.285	0.464	0.656	1.759	1.175
323	0.489	0.259	0.140	0.241	0.431	0.629	1.438	0.9488

Table 2. Determination of K_2 in accordance with equation (24) and (2) as a function of temperature calculated from solution of initial composition: $[Fe^{3+}] = 5 \times 10^{-4}$ mol dm^{-3} and $[HL] = 0.2$ mol dm^{-3}

Figure 5 shows the data of table 2 plotted in accordance with equation (16) assuming that the values of ΔH^o and ΔS^o are temperature-independent over the range of temperatures considered. This then enables the determination of the standard enthalpy and entropy of formation of the bisacetohydroxamatoiron(III) complex from the monoacetohydroxamatoiron(III) complex and acetohydroxamic acid; $\Delta H^o = -17.09$ kJ mol^{-1} and $\Delta S^o = -49.7$ J mol^{-1} K^{-1}. The negative values obtained for both parameters indicates that the formation of the bisacetohydroxamatoiron(III) complex is exothermic and enthalpically driven, as was the case for the monoacetohydroxamatoiron(III) complex.
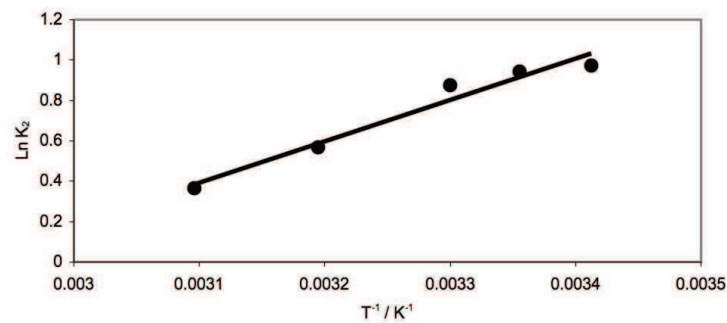

Fig. 5. LnK_2 vs. T^{-1} for the formation of the bisacetohydroxamatoiron(III) complex. Regression line : $Ln(K_2) = 2055T^{-1} - 5.982; R^2 = 0.9619$

3.4.3 Extinction coefficient determination

The deconvolution of the spectra recorded in this study, together with the determination of the concentration of the bishydroxamatoiron(III) complex in each solution, allows us to determine the extinction coefficient for this complex at $\lambda_{max} = 470$nm. This is done through the use of the ξ_2 equivalent of Beer's law shown in equation (17). The extinction coefficient for the bisacetohydroxamatoiron(III) complex was found to be $\epsilon_2 = 1650 \pm 150$ mol dm^{-3} cm^{-1}.

3.5 Thermodynamics of trisacetohydroxamatoiron (III) complex formation

Using a strategy analogous to that used in the determination of K_2, it is possible to determine a value of K_3. Again, to simplify the mathematics, solutions of acetohydroxamic acid and iron(III) are prepared that contain a mixture of the bis- and trisacetohydroxamatoiron(III) complex only (i.e. ξ_1 is negligible compared to ξ_2 and ξ_3). It is worth noting here that solutions containing only the trisacetohydroxamatoiron(III) complex, which would further simplify the mathematical treatment of the data, would require the dissolution of a quantity of acetohydroxamic acid at a level above its water solubility making this option unviable. Figure 6 shows a typical spectra recorded for this experiment, where the signals from the bis- and trisacetohydroxamatoiron(III) complexes have been deconvoluted using the methodology described in section 3.4.1, i.e. by subtracting the normalised averaged spectra of FeL_2^+ from the real solution spectra in order to isolate that of the trisacetohydroxamatoiron(III) complex. The literature value of the wavelength of maximum absorption for the latter (λ_{max} = 420nm) (Renshaw et al.,2002) was used to determine the value of the scaling factor.
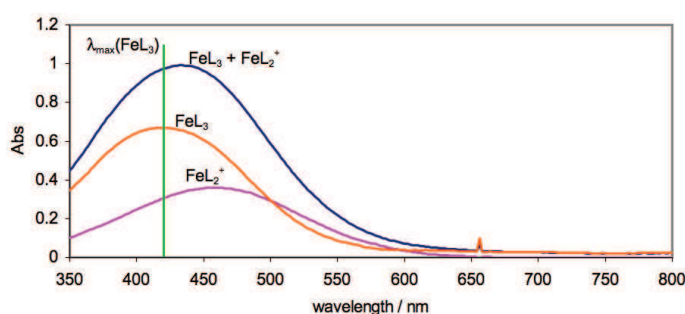

Fig. 6. Typical deconvolution of a spectrum recorded for a solution containing 4×10^{-4} mol dm^{-3} iron(III) and 6.3 mol dm^{-3} HL at pH = 0.84, T = 298K

Again, the formation of the trisacetohydroxamatoiron(III) complex may be envisaged as a series of reactions taking place sequentially and resulting in the formation of complexes of increasing order or as a one step process resulting in the formation of a mixture of complexes. Whilst the former would result in a simpler mathematical expression, the latter explicitly takes into account the presence of all species. It does however necessitate the definition of a thermodynamic equilibrium constant for the formation of the trisacetohydroxamatoiron(III) complex from iron(III) and acetohydroxamic acid, K_3':

$$K_3' = K_1 K_2 K_3 = \frac{[FeL_3][H^+]^3}{[Fe^{3+}][HL]^3} \tag{25}$$

which may be expressed as a function of the equilibrium concentrations defined in equations (5)-(10) and under conditions where ξ_1 is negligible as:

$$K_3' = \frac{\xi_3 \left([H^+]_i + 2\xi_2 + 3\xi_3\right)^3}{\left([Fe^{3+}]_i - \xi_2 - \xi_3\right)\left([HL]_i - 2\xi_2 - 3\xi_3\right)^3} \tag{26}$$

Using the extinction coefficient for the bisacetohydroxamatoiron(III) complex and the deconvoluted spectra for the mixture of bis- and trisacetohydroxamatoiron(III), it is possible to extract values of ξ_2 for all data recorded, leaving equation (26) with only two unknown parameters (K_3' and ξ_3). Using the approach used in the determination of K_2 and K_1, it is possible to use the spectra recorded for two samples at the same temperature but different

pH values to extract values of ξ_3 and enable the determination of K_3. Here the ratio of concentration is defined as z:

$$\frac{\xi_{3_1}}{\xi_{3_2}} = \frac{Abs_1}{Abs_2} = z \tag{27}$$

where the very last digit of the subscript in each term refers to the arbitrarily attributed experiment number. This results in the establishment of the soluble system of two equations with two unknowns:

$$K_3' = \frac{\xi_{3_1}\left([H^+]_{i_1} + 2\xi_{2_1} + 3\xi_{3_1}\right)^3}{\left([Fe^{3+}]_{i_1} - \xi_{2_1} - \xi_{3_1}\right)\left([HL]_{i_1} - 2\xi_{2_1} - 3\xi_{3_1}\right)^3} \tag{28}$$

$$K_3' = \frac{z\xi_{3_1}\left([H^+]_{i_2} + 2\xi_{2_2} + 3z\xi_{3_1}\right)^3}{\left([Fe^{3+}]_{i_2} - \xi_{2_2} - z\xi_{3_1}\right)\left([HL]_{i_2} - 2\xi_{2_2} - 3z\xi_{3_1}\right)^3} \tag{29}$$

which may be equated and re-arranged to yield the 8th order polynomial expression:

$$\xi_{3_1}\left([H^+]_{i_1} + 2\xi_{2_1} + 3\xi_{3_1}\right)^3\left([Fe^{3+}]_{i_2} - \xi_{2_2} - z\xi_{3_1}\right)\left([HL]_{i_2} - 2\xi_{2_2} - 3z\xi_{3_1}\right)^3 -$$
$$z\xi_{3_1}\left([H^+]_{i_2} + 2\xi_{2_2} + 3z\xi_{3_1}\right)^3\left([Fe^{3+}]_{i_1} - \xi_{2_1} - \xi_{3_1}\right)\left([HL]_{i_1} - 2\xi_{2_1} - 3\xi_{3_1}\right)^3 = 0 \tag{30}$$

Once again, an analytical solution to equation (30) may not be found trivially, but it may be computed by generating a spreadsheet calculating the value of the expression at the lefthand side of equation (30) as a function of ξ_{3_1}. The roots of equation (30) are then inspected and the single answer corresponding to a meaningful value of ξ_{3_1} (i.e. $0 < \xi_{3_1} \leq [Fe^{3+}]_{i_1}$) taken as the equilibrium concentration of the trisacetohydroxamatoiron(III) complex. The values of ξ_2 are calculated from the deconvoluted spectra and the extinction coefficient of the bisacetohydroxamatoiron(III) complex.

Table 3 shows the values of the absorbance of the bis- and trisacetohydroxamatoiron(III) complex from the deconvoluted data, together with the calculated average and standard deviation values of K_3.

T/K	Abs$_{bis}$ @ 470nm			Abs$_{tris}$ @ 420nm			Average K_3	Standard Deviation
	pH=0.44	pH=0.84	pH=0.93	pH=0.44	pH=0.84	pH=0.93		
293	0.540	0.370	0.086	0.341	0.656	0.200	0.0151	0.0015
298	0.510	0.360	0.085	0.434	0.670	0.198	0.0179	0.0038
303	0.490	0.330	0.080	0.473	0.802	0.200	0.0222	0.0057
313	0.450	0.290	0.075	0.543	0.842	0.206	0.0274	0.0080
323	0.380	0.270	0.070	0.553	0.856	0.210	0.0323	0.0091

Table 3. Determination of K_3 in accordance with equation (30) as a function of temperature calculated from solution of initial composition: $[Fe^{3+}] = 4 \times 10^{-4}$ mol dm^{-3} and [HL]=6.3 mol dm^{-3}

Figure 7 shows the data of table 3 plotted in accordance with equation (16) assuming that the values of ΔH^o and ΔS^o are temperature-independent over the range of temperatures considered. This then enables the determination of the standard enthalpy and entropy of formation of the trisacetohydroxamatoiron(III) complex from the bisacetohydroxamatoiron(III) complex and acetohydroxamic acid, respectively $\Delta H^o = +19.74$

kJ mol^{-1} and ΔS^o = +32.9 J mol^{-1} K^{-1}. These values are both positive suggesting that the process is endothermic in nature and entropically driven, in contrast to the processes associated with the formation of the mono- and bisacetohydroxamatoiron(III) complexes. This has implication for the temperature-dependent speciation of the iron(III)-acetohydroxamic acid system which we shall return to shortly.
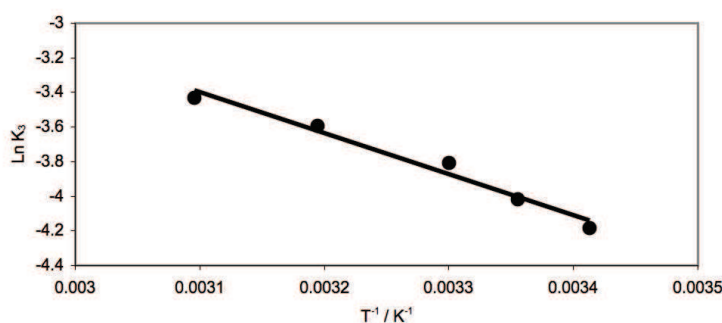

Fig. 7. LnK_3 vs. T^{-1} for the formation of the trisacetohydroxamatoiron(III) complex. Regression line : $Ln(K_3) = -2374T^{-1} + 3.961; R^2 = 0.9752$

3.5.1 Extinction coefficient determination

The deconvolution of the spectra recorded in this study, together with the determination of the concentration of the trishydroxamatoiron(III) complex in each solution, allows us to determine the extinction coefficient for this complex at λ_{max} = 420nm. This is done through the use of the ζ_3 equivalent of Beer's law shown in equation (17). The extinction coefficient for the trisacetohydroxamatoiron(III) complex was found to be ϵ_3 = 3630 $\pm$ 290 mol dm^{-3} cm^{-1}.

3.6 Temperature-dependent speciation of the iron (III) - acetohydroxamic acid system

With the temperature-dependent value of K_1, K_2 and K_3 determined, it is possible to generate a series of speciation diagrams for the Fe-AHA system as a function of pH, HL concentration (expressed as pHL=$-\log_{10}[HL]$) and temperature. These diagrams are generated by calculating the equilibrium concentrations of each of the iron(III)-containing species (Fe^{3+}, FeL^{2+}, FeL$_2^+$ and FeL$_3$) present in solution for a set of known starting conditions (i.e. [Fe^{3+}]$_i$, [HL]$_i$, [H$^+$]$_i$, and T) through the use of equations (1)-(3) and (5)-(10).

3.6.1 Speciation as a function of acidity

Figure 8 shows the speciation of the Fe-AHA system as a function of [HL] expressed as pHL at 293K for a range of pH values. As is to be expected from equations (1)-(3) an increase in pH (decrease in [H$^+$]) favours the formation of higher order complexes a direct result of LeChatelier's principle. It is important to stress that these speciation diagrams represent meaningful solution compositions up to a pH value of 2 as above this value iron(III) undergoes hydrolysis to form iron oxyhydroxides which are purposely overlooked in the calculation of these diagrams.

3.6.2 Speciation as a function of acetohydroxamic acid concentration

Figure 9 shows the speciation of the Fe-AHA system as a function of pH at 293K for a range of acetohydroxamic acid concentrations. Again as expected from equations (1)-(3) an increase in acetohydroxamic acid concentration results in the production of higher complexes due to LeChateliers principle.
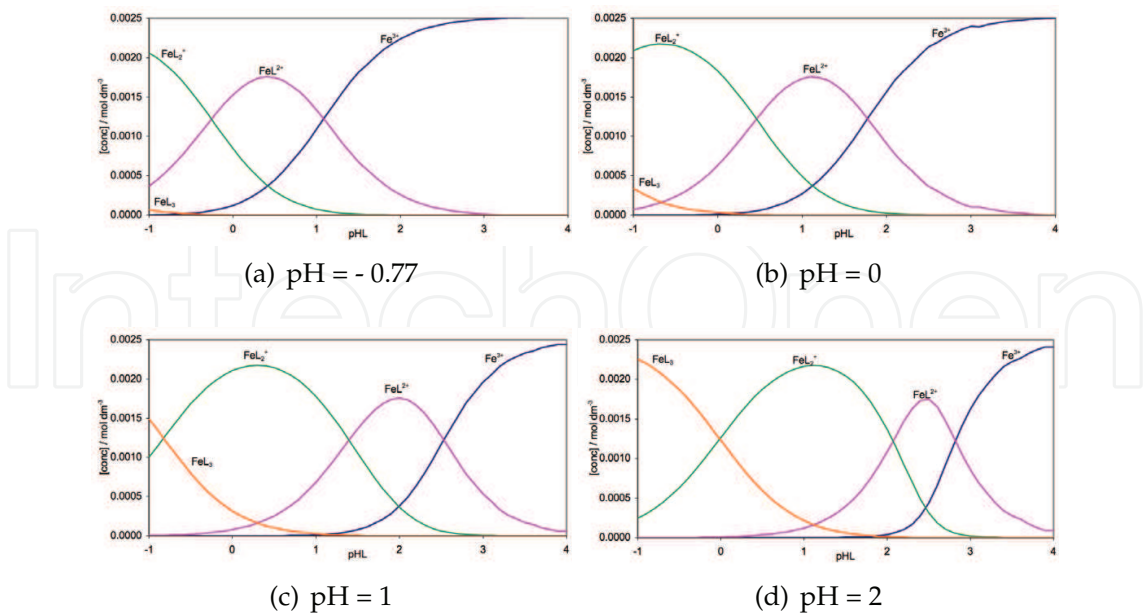
(a) pH = - 0.77

(b) pH = 0

(c) pH = 1

(d) pH = 2

Fig. 8. Speciation diagrams showing the concentration of Fe^{3+}, FeL^{2+}, FeL_2^+ and FeL_3 as a function of initial acetohydroxamic acid concentration (expressed as pHL) calculated for a total iron(III) concentration of 2.5×10^{-3} mol dm^{-3} at a temparature of 293K and pH values of -0.77, 0, 1 and 2 as per legend.

3.6.3 Speciation as a function of temperature

Figure 10 shows the speciation of the Fe-AHA system as a function of acetohydroxamic acid concentration expressed as pHL at pH = 1 for a range of temperatures. From this set of figures, it is apparent that an increase in temperature results in the production of free iron(III) and the trisacetohydroxamatoiron(III) complex at the expense of both the mono- and bisacetohydroxamatoiron(III) complexes. This is to be expected from the exothermic nature of the reaction producing the latter two compounds and the endothermic nature of the reaction resulting in the formation of the trisacetohydroxamatoiron(III) complex.

3.7 Verification of assumptions

During the course of this study a number of assumption have been made in order to simplify the mathematical treatment of the data collected. It is now necessary to return to these assumptions and verify that they are justified.

3.7.1 Determination of K_1

In the determination of the equilibrium constant for the formation of the monoacetohydroxamatoiron(III) complex an assumption was made that the concentrations of the bis- and trisacetohydroxamatoiron(III) complex were negligible when compared to the concentration of the monoacetohydroxamatoiron(III) complex. Figure 11 shows the speciation diagrams recorded in the conditions of the experiment at 293 and 323K, the temperature range boundaries. Under the conditions of the experiment, a maximum of 0.3% of all complexed iron(III) is present in the form of the bis- or trisacetohydroxamatoiron(III) complex, which strongly support our assumption that FeL^{2+} is the predominant Fe-AHA species in solution.
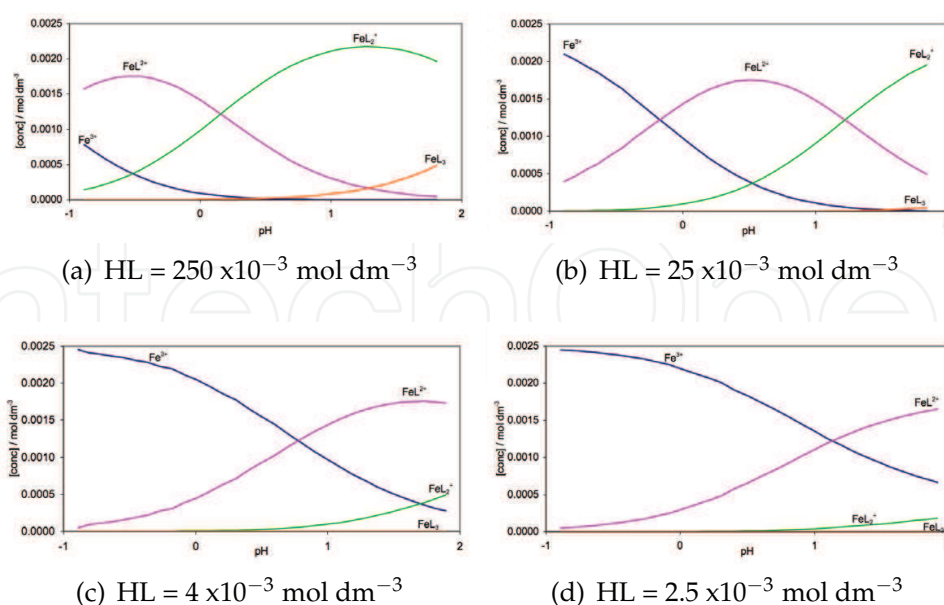
(a) HL = 250 x10^{-3} mol dm^{-3} (b) HL = 25 x10^{-3} mol dm^{-3}

(c) HL = 4 x10^{-3} mol dm^{-3} (d) HL = 2.5 x10^{-3} mol dm^{-3}

Fig. 9. Speciation diagrams showing the concentration of Fe^{3+}, FeL^{2+}, FeL_2^+ and FeL_3 as a function of pH calculated for a total iron(III) concentration of 2.5x10^{-3} mol dm^{-3} at a temparature of 293K and acetohydroxamic acid concentration of 250 x10^{-3}, 25 x10^{-3}, 4 x10^{-3}, 2.5 x10^{-3} mol dm^{-3} as per legend, corresponding to AHA:Fe ratios of 100:1, 10:, 1.6:1 and 1:1.

3.7.2 Determination of K_2

Figure 12 shows the speciation diagram for the Fe-AHA system calculated for the specific experimental conditions under which K_2 was determined. These confirm that a maximum of 2.7% of all complexed iron is present as the trisacetohydroxamatoiron(III) complex, validating the assumption that the mono- and bisacetohydroxamatoiron(III) complexes are the predominant species.

3.7.3 Determination of K_3

Figure 13 shows the speciation diagram for the Fe-AHA system calculated for the specific experimental conditions under which K_3 was determined. These confirm that a maximum of 2.5% of all complexed iron is present as the monoacetohydroxamatoiron(III) complex, confirming, as we assumed, that the bis- and trisacetohydroxamatoiron(III) complexes are the predominant species.

4. Conclusion

The thermodynamic constants for all three equilibria that obtain in the iron(III)-AHA system have been calculated and the associated enthalpies and entropies for the formation of these complexes have been determined. These are summarised in Table 4 together with the molar absorptivity for each of the three complexes. These new values have been used to calculate speciation diagrams for the Fe-AHA system as a function of pH, AHA concentration and temperature.

Inspection of the molar absorptivities measured for all three complexes reveal that it increases as the number of ligands bound to the iron increases. This is thought to be in line with the
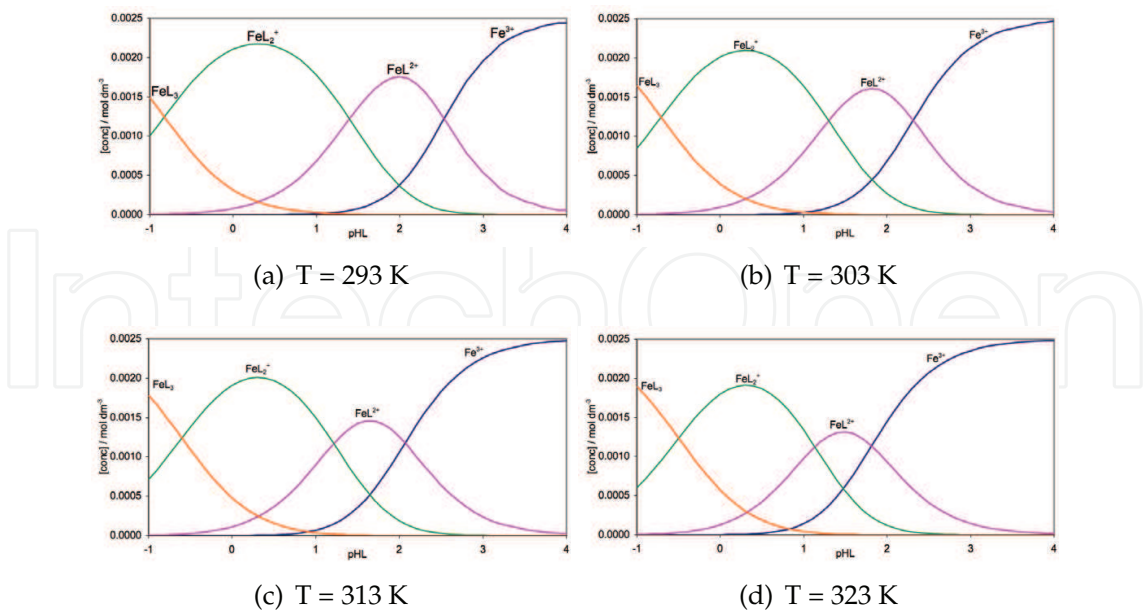
(a) T = 293 K   (b) T = 303 K

(c) T = 313 K   (d) T = 323 K

Fig. 10. Speciation diagrams showing the concentration of Fe^{3+}, FeL^{2+}, FeL_2^+ and FeL_3 as a function of acetohydroxamic acid concentration (expressed as pHL) calculated for a total iron(III) concentration of 2.5×10^{-3} mol dm^{-3} at pH = 1 and T = 293K, 303K, 313K, 323K as per legend.

complex formed	K @ 298K unitless	ΔH^o $kJmol^{-1}$	ΔS^o $Jmol^{-1}K^{-1}$	ϵ $dm^{-3}mol^{-1}cm^{-1}$
FeL^{2+}	42.64	-68.6	-199.0	1005
FeL_2^+	2.51	-17.09	-49.7	1650
FeL_3	1.18×10^{-2}	19.74	32.9	3630

Table 4. Thermodynamic data pertaining to the formation of the various iron(III)-AHA complexes

greater availability of ligands to contribute to the ligand-to-metal charge-transfer bands that dominate the absorption spectra of the Fe(III)-AHA system.

It is worth noting that both the entropy and enthalpy become progressively more positive as the number of bound ligands increases, i.e., complexation becomes enthalpically less favourable but entropically more favourable as the L:M ratio increases.

The change in entropy as individual reactions progress reflects a balance of two effects:

(i) an increase due to the chelate effect, as a result of the establishment of bonds in a 5-membered ring arrangement as the ligand binds to the metal centre while two water molecules from the inner solvation shell of iron(III) and a proton from the hydroxamic acid are released. This is accompanied by a re-ordering of the outer solvation sphere around the complex and a decrease in the overall charge on the complex.

(ii) a decrease due to the overall transfer of charge from the bulky Fe^{3+} ion to the much smaller proton leading to an increase in charge density and simultaneous solvent ordering around the charge.

In the formation of FeL^{2+}, process (ii) is presumably dominant but becomes less so as the ligand number increases due to the decrease in charge of the formed complex and associated
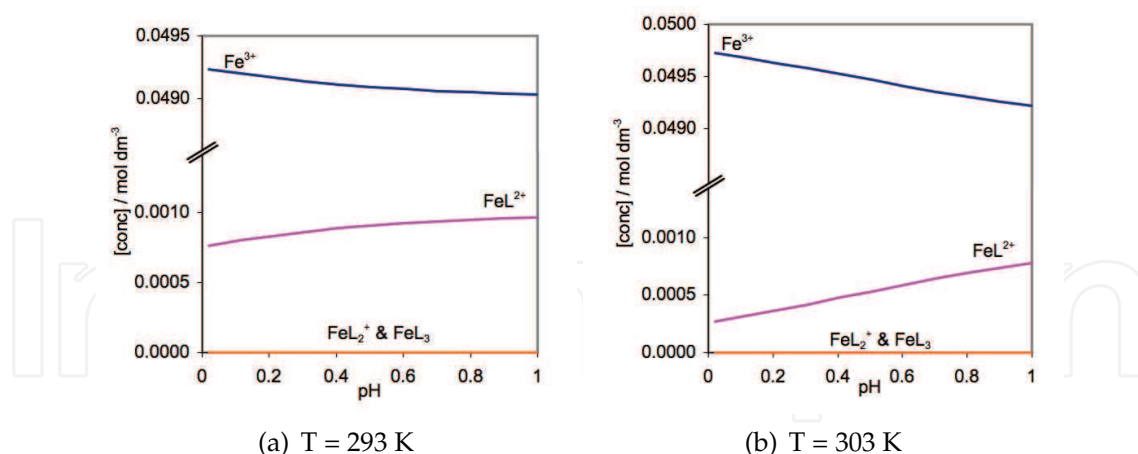
(a) T = 293 K   (b) T = 303 K

Fig. 11. Speciation diagrams showing the concentration of Fe^{3+}, FeL^{2+}, FeL_2^+ and FeL_3 as a function of acetohydroxamic acid concentration (expressed as pHL) calculated for the conditions under which K_1 was determined.

decreases in its influence on the ordering of the solvent. Thus as the influence of (ii) decreases, the impact of (i) becomes proportionately greater until it dominates and the complexation process exhibits an overall favourable formation entropy with the neutral FeL_3 complex.

The progression in enthalpy suggests that, as the degree of complexation increases, the energy balance between Fe-O bonds breaking (E_{bb}) and bonds forming (E_{bf}) changes from $|E_{bb}| < |E_{bf}|$ in the FeL^{2+} to $|E_{bb}| > |E_{bf}|$ in the FeL_3 complex, i.e., the replacement of two H_2O molecules by an AHA ligand becomes less favourable. This is presumably related to steric considerations as the hydroxamate ligand is much bulkier than the two water molecules it displaces. Thus, as the number of hydroxamato ligands around the metal increases, the resultant ligand-ligand repulsion forces increase, acting against the enthalpy gained by complexation.

The work carried out in this study supports the wider understanding of the behaviour of hydroxamic acids as chelating ligands for hard cations such as Fe(III), Pu(IV) and Np(IV), in particular the kinetics of hydrolysis of these ligands in the presence of such cations in the context of nuclear reprocessing and specifically the development of advanced reprocessing flowsheets. As such the determination of the thermodynamic equilibrium constants for the formation of the various Fe-AHA complexes, allows for our model of the kinetics of hydrolysis of hydroxamic acids in the presence of non-oxidising metal cations (Andrieux et al.,2007) to be extended to temperatures away from room temperature and determine the activation energy and pre-exponential factor associated with the hydrolysis processes, giving access to valuable mechanistic information. This work is currently ongoing in our laboratories and will be the subject of a forthcoming publication.

5. Acknowledgements
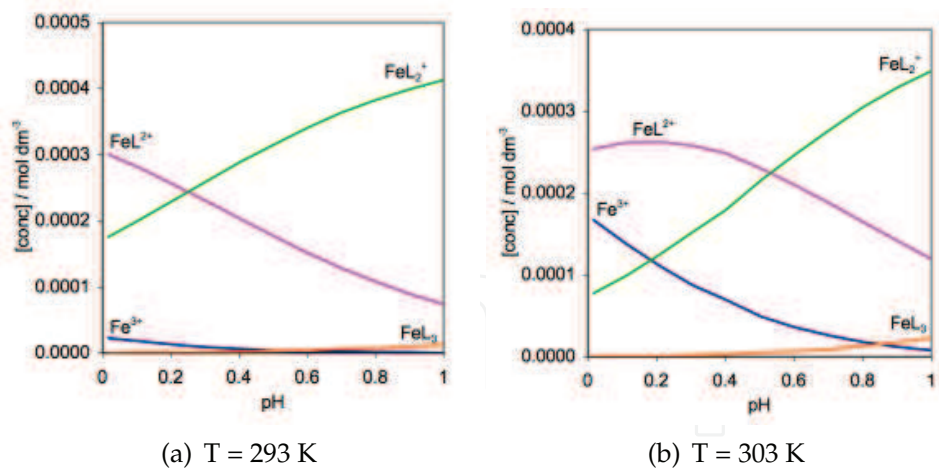
(a) T = 293 K   (b) T = 303 K

Fig. 12. Speciation diagrams showing the concentration of Fe^{3+}, FeL^{2+}, FeL_2^+ and FeL_3 as a function of acetohydroxamic acid concentration (expressed as pHL) calculated for the conditions under which K_2 was determined.
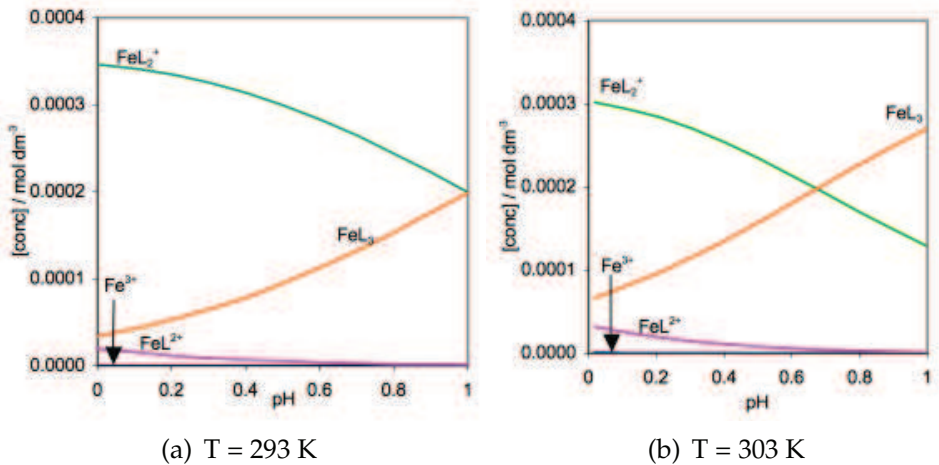

(a) T = 293 K   (b) T = 303 K

Fig. 13. Speciation diagrams showing the concentration of Fe^{3+}, FeL^{2+}, FeL_2^+ and FeL_3 as a function of acetohydroxamic acid concentration (expressed as pHL) calculated for the conditions under which K_3 was determined.

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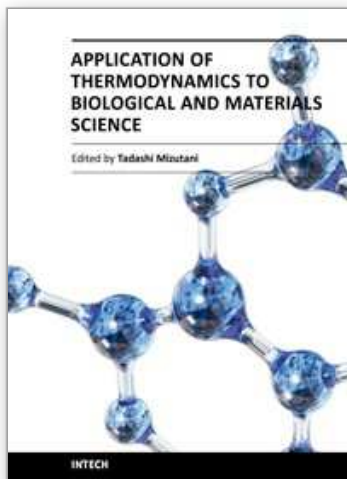
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Edited by Prof. Mizutani Tadashi

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