

# The Iron(III)-Chloride System. A Study of the Stability Constants and of the Distribution of the Tetrachloro Species between Organic Solvents and Aqueous Chloride Solutions

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On the basis of our own as well as other authors' spectrophotometric measurements we obtained a set of consecutive stability constants for the tetrachloroferrate(III) ion in HCl solutions. The fourth consecutive constant  $K_4$  was also estimated for concentrated LiCl and CaCl<sub>2</sub> solutions. The constants were corrected to ionic strength zero on the basis of some simplifying assumptions.

The spectra of the four chloro complexes were estimated from the data for HCl solutions. The spectra of the trichloro and tetrachloro complexes in strong LiCl and CaCl<sub>2</sub> solutions were also measured. The spectrum of the trichloro complex in HCl solutions showed some similarity to that of iron(III)-chloride in ether and probably corresponds to a transition form intermediate between octahedral and tetrahedral configuration.

The partition coefficients for distribution between HCl, LiCl-solutions and dibutylether or octan-2-ol were determined over a wide range of concentrations and HFeCl<sub>4</sub>, aq (H<sub>3</sub>O<sup>+</sup>, FeCl<sub>4</sub><sup>-</sup>) is found to be the only species extracted. The data were consistent with the stability constants, and the estimated salting-out coefficients for the tetrachloro iron(III)-acid were found to be proportional to the chloride concentration.

Measurements of the iron (III)/iron(II) redox potentials showed that iron(II) also forms a tetrachloro complex at sufficiently high LiCl and CaCl<sub>2</sub> concentrations.

The stability constants in the iron(III)-chloride system have been studied by several authors.<sup>1–8</sup> Rabinowitch and Stockmayer<sup>3</sup> determine spectrophotometrically values for  $K_1$  and  $K_2$  corrected to ionic strength zero. Gamlen and Jordan<sup>4</sup> have shown spectrophotometrically that the tetrachloroferrate(III) ion is the highest chloro complex present in hydrochloric acid solutions, and they estimated values for the constants  $K_3$  and  $K_4$  corrected to ionic strength zero in the same way as

described by Bjerrum.<sup>5</sup> In the present work  $K_4$  was estimated spectrophotometrically in strong HCl, LiCl and CaCl<sub>2</sub> solutions in the concentration range in which the tri- and tetrachloro complexes dominate.  $K_3$  was estimated for HCl solution in a concentration range in which the dichloro complex is also present. Our values for  $K_4$  are in good agreement with Gamlen and Jordan's value for this constant.

Other authors<sup>6,7</sup> have determined spectrophotometrically the first concentration stability constant for solutions having  $C_{\text{Fe(III)}} > C_{\text{Cl}^-}$ , and they have studied the great changes of the concentration constant at different high salt concentra-

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tions. Max Möller<sup>1</sup> determines a value for  $K_1$ , corrected to ionic strength zero from measurements of the iron(III)/iron(II) redox potentials under the assumption that the iron(II) ion does not form chloro complexes. Olerup<sup>2</sup> has shown that this assumption is not correct, and has determined by spectrophotometric and emf measurements the concentration constants for both iron(II) and iron(III)-chloride complexes in 2 M molar perchloric acid. Sekine and Tetuka,<sup>8</sup> like Olerup have determined the constants in a nearly constant perchlorate medium with  $[H^+] = 1.0$  M,  $[Na^+] = 3.0$  M. They estimated the stability constants from distribution experiments with the nonyltrifluoroacetone in carbon tetrachloride.

The extraction of iron(III) from hydrochloric acid solutions by diethylether forms the basis of an analytical procedure<sup>9</sup> which has been in use for nearly a century and many authors<sup>10-19</sup> have studied the distribution of iron(III) between hydrochloric acid solutions and various organic solvents. However, the strong increase in the solubility of iron(III) with increasing HCl concentration has not been fully explained by the former investigators.

In the present work we measured the partition coefficients for the distribution between acidic lithium chloride solution (in most cases with  $C_{HCl} = 0.10$  M) and octan-2-ol or dibutylether. The partition coefficients were measured over a wide range of lithium chloride activities varying from 7 to 630. The extracted species was in all cases  $HFeCl_4$ , aq, most probably present as the ion pair  $H_3O^+$ ,  $FeCl_4^-$ . The variation in the partition coefficients is quantitatively consistent with the stability constants, and the salting-out coefficients for the tetrachloroiron(III) acid were found to be proportional to the lithium chloride concentration.

## Experimental

**Reagents and solutions.** The lithium chloride, calcium chloride and iron-free 37% hydrochloric acid employed were of analytical grade or of good commercial quality. Octan-2-ol with  $d_4^{20} = 0.820$  was obtained from Merck-Schuchardt, and di-n-butylether with boiling point 140–42°C was purchased from Fluca. A stock solution of  $FeCl_3 \cdot 6H_2O$  in 0.1 M  $HClO_4$  was analysed by Zimmermann-Reinhardt permanganate titration<sup>20</sup> and also by Volhard titration. An oxygen-free stock

solution of Mohr's salt  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$  was used for the iron(III), iron(II) redox potential measurements. The various solutions were prepared in volumetric flasks by adding from burettes or pipetting from stock solutions. In order to eliminate the possibility of a photochemical reduction of iron(III) especially in strong hydrochloric acid medium,<sup>13</sup> the solutions were protected from direct sunlight and used shortly after their preparation.

**Partition coefficients.** Octan-2-ol and di-n-butylether have low vapour pressures and are practically insoluble in water, and for these reasons were chosen for the distribution experiments. A considerable amount of hydrogen chloride is extracted from strong hydrochloric acid solutions by ethers<sup>12</sup> and by octanol, and it was therefore decided to study the distribution using LiCl solutions with varying concentrations of HCl, also in order to obtain more reasonable values for the partition coefficient for the extracted iron(III). Lithium chloride is practically insoluble in ethers and less than 1% of LiCl is extracted from concentrated lithium chloride solutions by octanol.

In the distribution experiments, equal volumes of the organic solvent and the aqueous solution were normally shaken together in a separating funnel at 25°C. Equilibrium was established within 10–15 minutes.<sup>12</sup> The two liquid phases separated easily, and only in a few cases was it necessary to filter the solutions as a result of emulsion formation.

The solutions were analysed spectrophotometrically. Denoting the absorbance of the initially prepared iron(III)-chloride solution by  $A_{aq}^o$ , and that of the aqueous solution after shaking with the organic phase by  $A_{aq}$ , then the partition coefficient  $K_D$  is given by the expression

$$K_D = \frac{C_{Fe(III)}(org)}{C_{Fe(III)}(aq)} = \frac{A_{aq}^o - A_{aq}}{A_{aq}} \times \frac{V_{aq}}{V_{org}},$$

where  $V_{aq}$  is the volume of the aqueous and  $V_{org}$  of the organic phase. Denoting the initial iron(III) concentration in the aqueous solution by  $C_{Fe(III)}^o$ , then the iron(III) concentration in the organic phase is given by the expression

$$C_{Fe(III)}(org) = C_{Fe(III)}^o \times \frac{A_{aq}^o - A_{aq}}{A_{aq}} \times \frac{V_{aq}}{V_{org}},$$

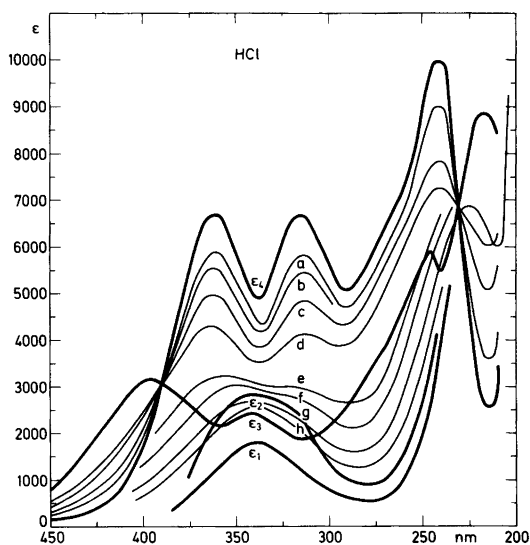


Fig. 1.  $\epsilon, \lambda$ -spectra of  $0.1954 \times 10^{-3}$  M iron(III) in hydrochloric acid solutions. Curves: a 11.51 M, b 10.50 M, c 9.50 M, d 8.49 M, e 5.99 M, f 4.99 M, g 4.03 M and h 3.02 M.

The estimated absorption curves for the individual species are shown with heavily drawn lines. Those for tetrachloro- ( $\epsilon_4$ ) and trichloroferrate(III) ( $\epsilon_3$ ) are estimated from the calculated fractions of tetrachloro complex tabulated in Table 1.

The absorption curve for the dichloro complex ( $\epsilon_2$ ) is estimated by using the calculated distribution of the complexes tabulated in Table 4, especially making use of curves g and h. The absorption curve for the monochloro complex ( $\epsilon_1$ ) is reproduced from a paper by Heistand and Clearfield.<sup>7</sup>

so that the molar absorbances of the species in the organic layer can also be determined.

*Spectrophotometric measurements* were made on a Cary 118 spectrophotometer at 24–25°C. The spectra were recorded from 500 nm to 210 nm. In certain cases the absorbances were also read directly from the spectrophotometer. Owing to the

high UV absorption of the solutions most of the measurements were made in 0.1 cm silica cells, the reference cell being filled with a corresponding iron(III)-free solution.

*Emf measurements.* The iron(III)/iron(II) redox potentials in weakly acidic lithium and calcium chloride solution with  $C_{\text{Fe(III)}} = C_{\text{Fe(II)}} = 0.01$  M were measured with a gold electrode using a thermostatted jacketed vessel with liquid junction connection to a saturated KCl-calomel electrode. No correction for diffusion potentials was made.

### The stability constants

The  $\epsilon, \lambda$ -absorption spectra of a series of hydrochloric acid solutions (with  $C_{\text{Fe(III)}} = 1.954 \times 10^{-3}$  M) are shown in Fig. 1. The family of curves for concentrations between 8 and 12 M is seen to have two isosbestic points confirming the existence of an equilibrium between only two species. The complexes present in this concentration range are the trichloroferrate(III) and tetrachloroferrate(III) ions as was assumed by Gamlen and Jordan.<sup>4</sup> It is therefore possible under simplified conditions to calculate  $K_4$ , the fourth consecutive constant in the iron(III) system. In the same way as Gamlen and Jordan<sup>4</sup> we have approximated this constant by the expression:

$$K_4 = \frac{[\text{FeCl}_4^-]}{[\text{FeCl}_3] \times a_{\text{Cl}^-}},$$

where  $a_{\text{Cl}^-}$  is taken to be equal to  $\gamma_{\text{HCl}}^c C_{\text{HCl}}$ .

In a system with isosbestic points three absorption curves are required to calculate the equilibrium constant. Using the curves a, b and c with the molar absorbances  $\epsilon_a$ ,  $\epsilon_b$  and  $\epsilon_c$  (decreasing in that order), and denoting the corresponding chloride activities ( $a_{\text{Cl}^-}$ )<sub>a</sub>, ( $a_{\text{Cl}^-}$ )<sub>b</sub>, ( $a_{\text{Cl}^-}$ )<sub>c</sub>, the constant  $K_4$  can be calculated directly from the previously derived expression<sup>21</sup>:

$$\frac{(a_{\text{Cl}^-})_a - (a_{\text{Cl}^-})_b + \{(a_{\text{Cl}^-})_a (a_{\text{Cl}^-})_c - (a_{\text{Cl}^-})_b (a_{\text{Cl}^-})_c\} K_4}{(a_{\text{Cl}^-})_a - (a_{\text{Cl}^-})_c + \{(a_{\text{Cl}^-})_a (a_{\text{Cl}^-})_b - (a_{\text{Cl}^-})_b (a_{\text{Cl}^-})_c\} K_4} = \frac{\epsilon_a - \epsilon_b}{\epsilon_a - \epsilon_c}$$

In our case four absorption curves are available for the calculation of  $K_4$  and we have employed the combinations I (a, c, d) and II (b, c, d). The

results of the calculation are given in Table 1. The values for the molar absorbance expressions shown in the table are mean values with esti-

Table 1. Estimation of  $K_4$  from the isosbestic system of absorption curves in concentrated hydrochloric acid.

I (a,c,d)  $(\epsilon_a - \epsilon_c)/(\epsilon_a - \epsilon_d) = 0.615 \pm 0.034$

II (b,c,d)  $(\epsilon_b - \epsilon_c)/(\epsilon_b - \epsilon_d) = 0.461 \pm 0.025$

	HCl	$C_{\text{HCl}}$	$\gamma_{\text{HCl}}^{(c)}$	$a_{\text{HCl}}$	$\alpha_4(\text{I})$	$\alpha_4(\text{II})$
I	a	11.51	48.6	560	0.803	(0.821)
II	b	10.50	32.0	336	(0.710)	0.734
I, II	c	9.496	21.1	200	0.593	0.621
I, II	d	8.489	13.9	118	0.461	0.492

I (a,c,d) leads to:  $\log K_4 = -2.14 \pm 0.19$

II (b,c,d) leads to:  $\log K_4 = -2.09 \pm 0.18$

Average:  $K_4 = 0.0078$

$\log \gamma_{\text{HCl}}^{(c)} \sim -0.45 + 0.187 C_{\text{HCl}}$

mated uncertainties calculated from the molar absorbances at sixteen selected wavelengths throughout the entire spectrum. The values of  $\gamma_{\text{HCl}}^{(c)}$  used to calculate the chloride activities are taken from Robinson and Stoke's data<sup>22</sup> derived from isopiestic measurements of  $\gamma_{\text{HCl}}^{(m)}$  up to high molalities. Our mean value of  $K_4 = 0.0078$  ( $\log K_4 = -2.11 \pm 0.18$ ) is in fair agreement with the value  $K_4 = 0.0105$  estimated by Gamlen and Jordan.<sup>4</sup> These authors also estimated a value for  $K_3$  by a graphical method. However, their value of  $K_3 = 0.73$  appears to be suspiciously high.

Several authors<sup>2,3,8</sup> have determined some of the concentration constants in almost constant salt media (see Table 3), but only Rabinowitch and Stockmayer<sup>3</sup> have corrected their constants determined in 1 M HCl, ClO<sub>4</sub> to zero ionic strength, and their value of  $K_3 = 0.10$  is much lower than that of Gamlen and Jordan. The Rabinowitch and Stockmayer values for  $K_1$  and  $K_2$  seem to be reliable, and we have therefore com-

bined their values ( $K_1 = 30$  and  $K_2 = 4.5$ ) with our value for  $K_4$  and obtained by trial and error the value  $K_3 (= 0.15)$ . With the two sets of constants obtained in this way we have calculated (Table 4) the fractions of the different iron(III)

 Fig. 2.  $\epsilon, \lambda$ -spectra of  $0.1954 \times 10^{-3}$  M iron(III) in lithium chloride and calcium chloride solutions.

Upper figure. Curves in LiCl: a 11.62 M, b 9.60 M, c 8.59 M, d 6.03 M, e 4.02 M and f 1.005 M.

Lower figure. Curves in CaCl<sub>2</sub> ( $C_{\text{Cl}^-}$ ): a 10.63 M, b 9.106 M, c 8.098 M, d 6.003 M, e 4.01 M and f 1.008 M.

The absorption curves for the tetrachloro- ( $\epsilon_4$ ) and trichloroferrate(III) ( $\epsilon_3$ ) are estimated from the fractions of these complexes calculated from  $\gamma_{\text{Cl}^-}$  (tabulated in Table 2).

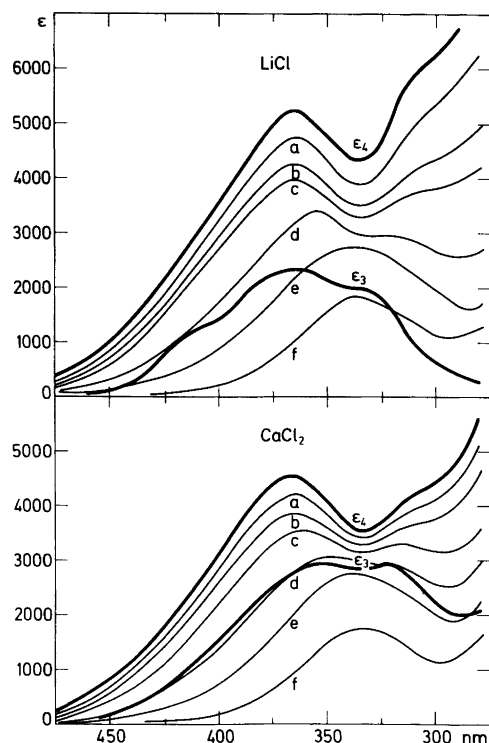


Table 2. Estimation of  $K_4$  from the absorption spectra in concentrated lithium- and calcium chloride solutions.

$$\text{LiCl: } (\epsilon_a - \epsilon_b)/(\epsilon_a - \epsilon_c) = 0.606 \pm 0.046$$

Sol	$C_{\text{LiCl}}$	$\gamma_{\text{LiCl}}^c$	$a_{\text{LiCl}}$	$\alpha_4$	$\alpha_3$
a	11.62	44.7	519	0.776	0.224
b	9.60	20.4	196	0.567	0.433
c	8.59	13.2	113	0.431	0.569

$$\log \gamma_{\text{LiCl}}^c \sim -0.53 + 0.190 C_{\text{Cl}^-}, \quad \log K_4 = -2.17 \pm 0.25, \quad K_4 = 0.0068$$

$$\text{CaCl}_2: (\epsilon_a - \epsilon_b)/(\epsilon_a - \epsilon_c) = 0.496 \pm 0.026$$

Sol	$C_{\text{Cl}^-}$	$\gamma_{\text{CaCl}_2}^c$	$a_{\text{Cl}^-}(\text{I})$	$\alpha_4(\text{I})$	$\alpha_4(\text{II})$
a	10.63	17.6	187	0.849	0.888
b	9.106	9.0	82	0.711	0.757
c	8.098	5.5	44.5	0.572	0.624

$$\begin{aligned} \text{(I) } \log K_4 &= -1.52 \pm 0.16 \\ \text{(I) } \log \gamma_{\text{CaCl}_2}^c &\sim -0.90 + 0.187 C_{\text{Cl}^-}, K_4 = 0.030 \\ \text{(II) } \log F &= -0.50 + 0.22 C_{\text{Cl}^-}, K_4 = 0.0108 \end{aligned}$$

chloro complexes in 5.99 M and 8.49 M HCl; these are the concentrations which correspond to the absorption curves e and d in Fig. 1. These calculations show that the fraction of the dichloro complex calculated using the constants of Gamlen and Jordan are so small that the curve e should still belong to the family of curves going through the isosbestic points which is far from being the case. The calculation using our set of constants shows that the solution corresponding to curve e should contain 16 per cent of the dichloro complex which is much more reasonable. Finally, a convincing support for the validity of our set of constants is provided by the fact that the calculated value of  $\alpha_4$  (= 0.475) in 8.49 M HCl (curve d) is in excellent agreement with the values calculated in Table 1 by analysis of the isosbestic system. It can further be seen that a content of 2–3 per cent of the dichloro complex does not influence appreciably the fact that curve d still belongs to the family of isosbestic curves.

The stability constant  $K_4$  was also estimated from the  $\epsilon, \lambda$ -spectra of the series of iron(III) solution in lithium and calcium chloride media (Fig. 2). These systems have no isosbestic points, but a closer examination of the absorption curves for

high chloride concentrations shows that they correspond closely to the presence of a mixture of only two complexes. The necessary data and the result of the calculations of three solutions with  $C_{\text{Cl}^-} > 8$  M are shown in Table 2. The calculated value of  $K_4$  in the lithium chloride solution agrees well with that calculated for the hydrochloric acid solutions. On the other hand, the value ( $K_4 \sim 0.03$ ) calculated for the  $\text{CaCl}_2$  solutions with  $a_{\text{Cl}^-} = \gamma_{\text{CaCl}_2}^c C_{\text{Cl}^-}$  is much too high. However, when using the empirical expression for the logarithm to the activity coefficient<sup>5,25</sup>

$$\log F = A + B \times C_{\text{Cl}^-},$$

with  $A = 0.5$ , it is sufficient to insert a value for  $B$  of 0.22 (instead of 0.19) in order to obtain the correct order for  $K_4 \sim 0.01$  (see Table 2). For comparison it can be mentioned that a similar value ( $B = 0.21$ ) was estimated in the  $\text{CuCl}_2$ ,  $\text{CaCl}_2$  system<sup>5,24</sup> whereas a much lower value ( $B = 0.13$ ) was estimated for the  $\text{CoCl}_2$ ,  $\text{CaCl}_2$  system.<sup>25</sup>

We may conclude that our use of  $a_{\text{Cl}^-} = \gamma^c C_{\text{Cl}^-}$  as a measure of the activity function in strong chloride solutions is a reasonably good approximation for the iron(III) hydrochloric acid and -lithium chloride systems, but does not work so well for the iron(III)-calcium chloride system.

### On the tetrachloroferrate(II)

As shown by Olerup<sup>2</sup> iron(II) forms somewhat weaker chloro complexes than iron(III), but it is as yet unknown how far complex formation proceeds in strong chloride solutions. In order to explore this we measured the iron(III)/iron(II) redox potentials in concentrated lithium and calcium chloride solutions. The results of the measurements are shown in Fig. 3 in which the redox potentials including diffusion potentials are plotted *versus* the logarithm of the chloride activity. For experimental details, see Experimental.

From the slopes of the potential curves

$$\frac{dE}{d \log a_{\text{Cl}^-}} = 0.059 (\bar{n}_{\text{Fe(III)}} - \bar{n}_{\text{Fe(II)}})$$

it is estimated that  $\bar{n}_{\text{Fe(III)}}$  in 6–8 M chloride solutions is about 0.5 higher than  $\bar{n}_{\text{Fe(II)}}$  in LiCl, and 0.3 higher than  $\bar{n}_{\text{Fe(II)}}$  in  $\text{CaCl}_2$  in this concen-

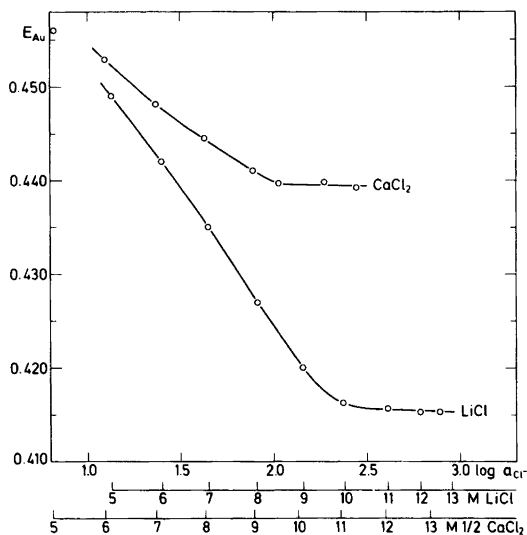


Fig. 3. Iron(III)/iron(II) redox potentials in chloride solutions with  $C_{\text{Fe(II)}} = C_{\text{Fe(III)}} = C_{\text{HCl}} = 0.01 \text{ M}$ , and with LiCl and CaCl<sub>2</sub> concentrations varying from about 5 N up to saturation measured with a gold electrode with liquid junction connection to a saturated KCl-calomel electrode. The potential in volt at 25°C is plotted as a function of the logarithm of the chloride activity ( $\log(\gamma^c \times C_{\text{Cl}^-})$ ). The abscissa also indicates the corresponding molar concentrations of lithium and calcium chloride.

tration range. The rather different values of the redox potential in the two chloride media indicate that considerable diffusion potentials are involved. However, it is remarkable that the redox potentials for both curves attain a constant value corresponding to  $\bar{n}_{\text{Fe(III)}} = \bar{n}_{\text{Fe(II)}}$  for chloride concentrations higher than 10–11 M. This provides some evidence that iron(II) is also present as a tetrachloroferrate(II) complex in sufficiently concentrated chloride solutions.

### Discussion of partition coefficients

Several authors<sup>10–14</sup> have analysed the ether solutions of iron(III) extracted from hydrochloric acid solutions and found that one mol of HCl and several mols of water accompanies the extraction of one mol FeCl<sub>3</sub>, indicating that the iron(III) is extracted as HFeCl<sub>4</sub>, aq probably present as the ion pair H<sub>3</sub>O<sup>+</sup>, FeCl<sub>4</sub><sup>-</sup> in the organic phase. At low iron concentration the partition coefficient  $K_D = C_{\text{Fe(III)}(\text{org})}/C_{\text{Fe(III)}(\text{aq})}$  is independent of the iron concentration, but increases due to polymerization in the ether phase for iron(III) concentrations somewhat higher than 10<sup>-3</sup> M.<sup>12–14</sup> For various reasons (as mentioned in Experimental)

Table 4. Calculated values for the fractions of the iron(III)chloro complexes present at hydrochloric concentrations corresponding to the absorption curves from d to h in Fig. 1.

Curve d:	$C_{\text{HCl}} 8.49 \text{ M}$ , $\gamma_{\text{HCl}}^{(c)} 13.9$ , $a_{\text{Cl}^-} 118.0$ .
This work	$\alpha_1 0.5 \times 10^{-5}$ , $\alpha_2 0.028$ , $\alpha_3 0.497$ , $\alpha_4 0.475$ , $\bar{n} 3.45$ .
Curve e:	$C_{\text{HCl}} 5.99 \text{ M}$ , $\gamma_{\text{HCl}}^{(c)} 4.68$ , $a_{\text{Cl}^-} 28.0$ .
This work	$\alpha_1 0.001$ , $\alpha_2 0.160$ , $\alpha_3 0.682$ , $\alpha_4 0.156$ , $\bar{n} 2.99$ .
G. and J. <sup>4</sup>	0.0003, 0.036, 0.744, 0.220, $\bar{n} 3.18$ .
Curve f:	$C_{\text{HCl}} 4.99 \text{ M}$ , $\gamma_{\text{HCl}}^{(c)} 3.09$ , $a_{\text{Cl}^-} 15.4$ .
This work	$\alpha_1 0.004$ , $\alpha_2 0.274$ , $\alpha_3 0.642$ , $\alpha_4 0.080$ , $\bar{n} 2.80$ .
Curve g:	$C_{\text{HCl}} 4.03 \text{ M}$ , $\gamma_{\text{HCl}}^{(c)} 2.09$ , $a_{\text{Cl}^-} 8.41$ .
This work	$\alpha_1 0.011$ , $\alpha_2 0.419$ , $\alpha_3 0.533$ , $\alpha_4 0.036$ , $\bar{n} 2.56$ .
Curve h:	$C_{\text{HCl}} 3.024 \text{ M}$ , $\gamma_{\text{HCl}}^{(c)} 1.46$ , $a_{\text{Cl}^-} 4.43$ .
This work	$\alpha_1 0.029$ , $\alpha_2 0.573$ , $\alpha_3 0.384$ , $\alpha_4 0.014$ , $\bar{n} 2.38$ .

Table 3. Reported values of consecutive stability constants in the iron(III)-chloride system.

Method	Temp.	Medium	K <sub>1</sub>	K <sub>2</sub>	K <sub>3</sub>	K <sub>4</sub>	References
dis	25°	[H <sup>+</sup> ]=1 M, [Na <sup>+</sup> ]=3 M	7.6	1.2	—	—	72 S and T <sup>8</sup>
emf/sp	20°	2 M HClO <sub>4</sub>	5.7	2.0	0.9	—	44 O <sup>2</sup>
sp	26.7°	1 M H(Cl, ClO <sub>4</sub> )	4.2	1.3	0.04	—	42 R and S <sup>3</sup>
sp	25°	0 corr.	(30)	4.5	0.10	—	42 R and S <sup>3</sup>
sp	20°	0 corr.	(30)	(4.5)	0.73	0.0105	53 G and J <sup>4</sup>
sp	25°	0 corr.	(30)	(4.5)	0.15	0.0078	85 Bj and L

Table 5. Partition coefficient determinations for the distribution of iron(III) between weakly acidic lithium chloride solutions and two different organic solvents.

Dibutylether							
$C_{LiCl}$	8.99	10.08	10.08	10.08	11.03	11.99	11.99
$C_{HCl}$	0.10	0.004	0.02	0.10	0.10	0.02	0.10
$K_D$	0.18	0.16	0.21	0.66	1.90	1.22	4.21
$\gamma_{LiCl}^c$	15.8	24.5	24.5	24.5	37.6	50.1	50.1
$\alpha_4$	0.50	0.64	0.64	0.64	0.738	0.808	0.808
Octan-2-ol							
$C_{LiCl}$	4.00	4.75	5.50	5.99	5.99	7.00	
$C_{HCl}$	0.10	0.10	0.10	0.002	0.10	0.10	
$K_D$	0.03	0.32	1.82	0.89	7.2	~99	
$\gamma_{LiCl}^c$	1.78	2.43	3.31	4.07	4.07	6.24	
$\alpha_4$	0.024	0.047	0.089	0.115	0.115	0.204	

Table 6. Test of the validity of the expression:

$$X = \log K_D - \log a_{LiCl} - \log \alpha_4 - k_s C_{LiCl}$$

Dibutylether					
$C_{LiCl}$	8.99	10.08	11.03	11.99	
$\log K_D$	-0.745	-0.180	0.279	0.624	
$\log a_{LiCl}$	2.16	2.40	2.62	2.79	
$\log \alpha_4$	-0.301	-0.194	-0.132	-0.093	
$X + k_s C_{LiCl}$	-2.604	-2.386	-2.209	-2.073	
$k_s = 0.2, X =$	-4.402	-4.402	-4.415	-4.471	
Octan-2-ol					
$C_{LiCl}$	4.00	4.75	5.50	5.99	7.00
$\log K_D$	-1.522	-0.495	0.260	0.857	1.996
$\log a_{LiCl}$	0.852	1.062	1.260	1.387	1.640
$\log \alpha_4$	-1.62	-1.328	-1.051	-0.939	-0.690
$X + k_s C_{LiCl}$	-0.754	-0.229	0.051	0.409	1.046
$k_s = 0.6, X =$	-3.154	-3.079	-3.249	-3.185	-3.154

the extraction of iron(III) in the present work was made with dibutylether and octan-2-ol from HCl, LiCl solutions with  $C_{Fe(III)} = 1.954 \times 10^{-3}$  and  $C_{HCl}$  varying from 0.002 M to 0.10 M. The results of these measurements are collected in Table 5. The values of  $\alpha_4$ , the fraction of tetrachloroferrate(III), are those calculated using the stability constants given in Table 2 and assuming  $\gamma_{LiCl}^c C_{LiCl}$  as the chloride activity.

The partition coefficients increase as expected with the hydrochloric acid concentration at constant lithium concentration. However, what especially interested us was to explain the strong increase in the partition coefficients with increasing lithium chloride concentration at constant hydrochloric acid concentration. Considering the various factors which must play a rôle it has been possible to give a quantitative explanation of this effect.

When the tetrachloroiron(III) acid is the only extracted species the partition coefficients must be proportional to both the fraction of tetrachloro complex and the hydrochloric acid activity. This activity must again, when the hydrochloric acid concentration is small and constant, be close to being proportional to the lithium chloride activity. Furthermore, a salting-out effect on the tetrachloro species must also play a rôle. According to the generally applied salting-out law  $\log K_D$  is proportional to the change in the salt concentration:

$$\Delta \log K_D = k_s \times \Delta C_{\text{LiCl}},$$

where  $k_s$  is the salting-out coefficient. According to these considerations the partition coefficient should be proportional to:  $\alpha_4 \times a_{\text{LiCl}} \times 10^{k_s C_{\text{LiCl}}}$ . This can be expressed in the relationship:

$$X = \log K_D - \log \alpha_4 - a_{\text{LiCl}} - k_s C_{\text{LiCl}},$$

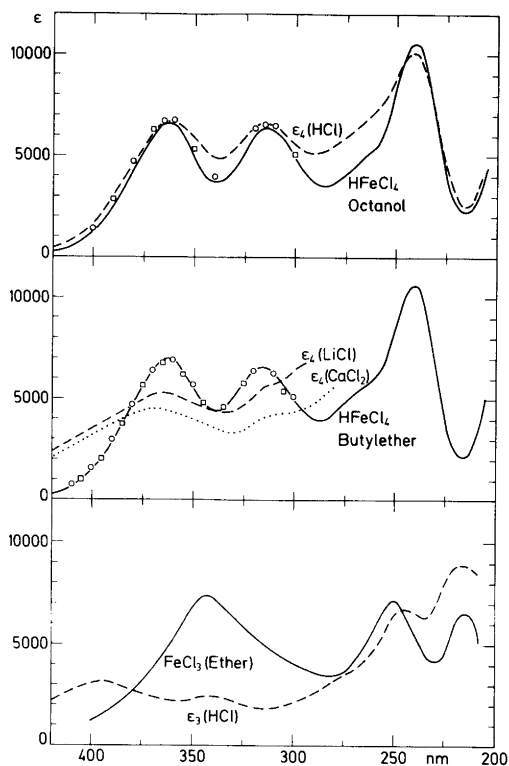
where  $X$  is a solubility constant.

In Table 6 the necessary data for  $C_{\text{HCl}} = 0.10 \text{ M}$  (from Table 5) are collected in order to test the derived relationship by choosing values for  $k_s$  in such a way that  $X$  assumes a constant value. The table shows that this can be fulfilled by choosing  $k_s \sim 0.2$  for dibutylether and  $k_s \sim 0.6$  for octan-2-ol, the uncertainty in  $k_s$  in both cases being about 10 per cent. These values appear to be of the correct order of magnitude. Thus  $k_s$  for the salting-out of tris(acetylacetonato)cobalt(III) into octan-2-ol has the following values: 0.48 for KCl, 0.41 for KBr and 0.19 for KSCN<sup>26</sup>. That the estimated value for the constant  $X$  is much higher for octan-2-ol than for dibutylether is of course a consequence of the much higher solubility of the tetrachloroiron(III) acid in the former solvent.

The results obtained provide quantitative confirmation of our ideas and considerations concerning the distribution ratios.

### Discussion of the spectra

Some of the spectra of the tetrachloroiron(III) acid in octan-2-ol and dibutylether determined in connection with our measurements of the partition coefficients in the foregoing section are shown in Fig. 4. The measured spectra are those for the species extracted from the hydrochloric acid containing lithium chloride solutions, and it



*Fig. 4. Upper part.*  $\epsilon, \lambda$ -spectra of tetrachloroiron(III) acid extracted with octan-2-ol from acid aqueous lithium chloride solutions with  $C_{\text{Fe(III)}} = 1.954 \times 10^{-3} \text{ M}$ . The full curve is the spectrum of the species extracted from 0.10 M HCl, 7.00 M LiCl, the points  $\circ\circ\circ$  are those of the species from 0.10 M HCl, 5.99 M LiCl, and the points  $\square\square\square$  are those of the species from 0.002 M HCl, 5.00 M LiCl. The dashed curve is the spectrum of tetrachloroferrate(III) ion in strong hydrochloric acid.

*Middle part.*  $\epsilon, \lambda$ -spectra of tetrachloroiron(III) acid extracted with dibutylether from acidic aqueous lithium chloride solutions. The full curve is the spectrum of the species extracted from 0.10 M HCl, 11.99 M LiCl, the points  $\square\square\square$  are those for the species from 0.10 M HCl, 11.03 M LiCl, whilst the points  $\circ\circ\circ$  are those for the species from 0.10 M HCl, 8.99 M LiCl. The dashed curve is the spectrum of tetrachloroferrate(III) ion in strong lithium chloride and the dotted curve is that in strong calcium chloride solutions.

*Lower part.* The full curve is the spectrum of anhydrous iron(III)chloride ( $10^{-3}$ – $10^{-5} \text{ M}$ ) in purified diethylether.<sup>18</sup> The dashed curve is the spectrum of trichloroferrate(III) ion in strong hydrochloric acid.



will be observed from the data plotted in Fig. 4 that the spectrum is the same in both organic solvents irrespective of the composition of the solutions from which they are extracted. This is as would be expected, but it is remarkable that a hydrochloric acid concentration as low as 0.002 is sufficient to maintain a constant spectrum in octan-2-ol.

The spectrum of the tetrachloroiron(III) acid is seen to have three bands in the UV at 365, 315 and 242 nm and a shoulder at 270 nm. This is in agreement with the findings of other authors<sup>14,15</sup> using different solvents.

It is interesting to compare the spectra of the tetrachloroiron(III) species in the organic solvents with those estimated for the tetrachloroferrate(III) ion in the aqueous solutions ( $\epsilon_4$  in Fig. 1 and Fig. 2). This comparison is made in Fig. 4, and it will be seen that the spectrum of the tetrachloro complex in strong hydrochloric acid solutions show a great similarity to that of the tetrachloro species in the organic solvents. The spectrum in hydrochloric acid is somewhat deformed but has maxima at the same wavelengths as the spectrum of the tetrachloro acid in the organic solvents. The spectrum in strong lithium chloride and especially strong calcium chloride solutions are much more strongly deformed and the maximum at 315 nm is reduced to being only a shoulder.

The UV spectrum of the tetrachlorocopper(II) complex is also strongly influenced by different salt-media.<sup>5,24</sup> The UV spectra of the particular chloride systems are charge-transfer spectra and as such are more strongly influenced by changes in the medium<sup>27</sup> than are the weaker ligand field bands in the visible region. The very weak iron(III) ligand field bands in the visible region have been used by Brady et al.<sup>17</sup> to demonstrate the existence of polymeric chloro complexes at high iron(III) concentrations. The Raman spectra show also that a network of octahedral iron(III)-chloride complexes are formed at high iron(III) concentrations.<sup>29</sup>

In Fig. 4 (lower part) the spectrum of the trichloroferrate(III) ion ( $\epsilon_3$  in Fig. 1) is compared with the spectrum of anhydrous iron(III) chloride in diethylether reproduced from a paper of Fajer and Linschitz.<sup>18</sup> McCusker and Kennard<sup>16</sup> have also measured the spectrum of the latter in various ethers. The iron(III)-chloride is present as a monomeric species in the ether solutions and dis-

plays absorption maxima at 342, 250 and ~220 nm.

The curve for  $\epsilon_3$  in hydrochloric acid is deformed but shows some similarity to that of the trichloroferrate(III) complex in ether. Thus the three absorption maxima in the UV are still observable but the band at 395 nm is characteristic only for the hydrochloric acid solutions. This band is practically non-existent in the lithium and calcium chloride solutions (see Fig. 2).

Magini<sup>28</sup> has confirmed by X-ray diffraction that the tetrachloro complex in strong hydrochloric acid solutions has a regular tetrahedral configuration with a Fe-Cl bond length of 2.25 Å. According to this author<sup>28</sup> the mono, di and trichloro species are octahedral chloro-aqua complexes, but this is not necessarily correct for the trichloro complex. A comparison of the absorption curves (in Fig. 1) for the mono and dichloro complex with that of the trichloro complex suggests that the latter species has a different configuration. It is most probably a more or less deformed transition form intermediate between the octahedral complex and the tetrahedral tetrachloro complex. Support for this proposal would be provided if further studies show that iron(III) chloride in ether has a trigonal bipyramidal configuration.

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