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# Chloro Complexes in Molten Salts. 5. Potentiometric and Spectrophotometric Study of Chloro Complexes Formed in KCl–AlCl$_3$–FeCl$_3$ at 300 °C

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By spectrophotometric and potentiometric measurements on KCl–AlCl$_3$–FeCl$_3$ at 300 °C it has been shown that the most likely reactions in the melt are (i) $AlCl_4^- + FeCl_4^- \rightleftarrows FeAlCl_7^- + Cl^-$ and (ii) $FeAlCl_7^- \rightleftarrows FeAlCl_6 + Cl^-$ with the p*K* values 6.75 ± 0.03 and 6.53 ± 0.06, respectively. On the basis of the self-dissociation constants for the solvent, the p*K* values for the exchange reactions (iii) $Al_2Cl_7^- + Fe_2Cl_7^- \rightleftarrows 2FeAlCl_7^-$ and (iv) $Al_2Cl_6 + Fe_2Cl_6 \rightleftarrows 2FeAlCl_6$ could be calculated. It was found for reaction iii that the distribution between Al(III) and Fe(III) was almost statistical with a p*K* value of −0.65 ± 0.06 but was displaced in the direction of homonuclear complex formation for reaction iv with a p*K* value of 0.2 ± 0.2. This p*K* value is rather similar to what has been found by others in the gaseous phase. Finally, the spectra of all of the found Fe(III) complexes have been calculated from measured spectra of KCl–AlCl$_3$–FeCl$_3$.

## Introduction

Very few experiments have been performed on dilute solutions of Fe(III) in molten salts. Gruen[1] reports that no spectral maxima were obtained above 400 nm for FeCl$_3$ in a LiNO$_3$–KNO$_3$ melt.

Balt[2] measured the spectrum of tetraphenylarsonium tetrachloroferrate(III) in the molten state, in the solid state, and in acetone (in this solvent the spectrum of tetraethylammonium tetrachloroferrate(III) was also measured) and concluded that he was dealing essentially with a tetrahedral $FeCl_4^-$ species. Cook and Dunn[3] suggested on the basis of vapor-pressure measurements and other measurements that the 1:1 mixture of NaCl–FeCl$_3$ in the molten state also contained the $FeCl_4^-$ anion.

Fairly recently[4] Andreasen and Bjerrum made potentiometric and spectrophotometric measurements on the KCl–FeCl$_3$ system. They concluded that the results could best be explained by two reactions: $2FeCl_4^- \rightleftarrows Fe_2Cl_7^- + Cl^-$ and $Fe_2Cl_7^- \rightleftarrows Fe_2Cl_6 + Cl^-$. At high chloride concentrations ([Cl$^-$] above ca. 0.4 M), they found that the only Fe(III) complex present was $FeCl_4^-$. An extrapolation of the data indicated that this should be true at least down to a chloride concentration of $10^{-2}$ M. The spectra of $FeCl_4^-$, $Fe_2Cl_7^-$, and $Fe_2Cl_6$ were also calculated from the measured spectra in connection with this work. It was concluded that the spectrum of $FeCl_4^-$ in KCl–FeCl$_3$ was rather similar to the spectra obtained by Balt[2] for $FeCl_4^-$.

## General Considerations

The formality, as previously,[5] is defined as the initial molar amount of one of the added substances (in the present work KCl, AlCl$_3$, and FeCl$_3$) dissolved in 1 L of the melt. The densities of the melts were calculated assuming that the mixtures of KFeCl$_4$ and KCl–AlCl$_3$ behaved ideally. This assumption will only give rise to a small error, as the amounts of KFeCl$_4$ were small compared to the amounts of KCl–AlCl$_3$. The densitites of KFeCl$_4$ and KCl–AlCl$_3$ were obtained from the work by Andreasen and Bjerrum[6] and Morrey and Carter,[7] respectively. The formal absorptivity is defined by $A/(lc')$, where $A$ is the absorbance corrected for the absorbance of cell and solvent, $l$ is the path length, and $c'$ is the formality.

Very important in connection with the determination of chloro complexes in chloroaluminate melts is the self-dissociation of the solvent. At the present stage of the examination of these KCl–AlCl$_3$ melts, the most likely reactions are clearly (1)–(3). The first two of these are now fairly well established,

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad (1)$$

$$Al_2Cl_7^- \rightleftarrows Al_2Cl_6 + Cl^- \qquad (2)$$

$$3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^- \qquad (3)$$

whereas the last one is somewhat in doubt.[8,9] The important thing, however, for the present work is not whether the last reaction (eq 3) is included in the calculations or not but whether a good or bad agreement is obtained between the measured and calculated pCl$^-$ values for the solvent. In the present paper we have only taken the first two equilibria into account since a better agreement is not obtained with three reactions.[9] In the present work p*K* values of 7.818 ± 0.006 and 6.83 ± 0.06 have been used for reactions 1 and 2, respectively.[9]

The present investigation is based on potentiometric and spectrophotometric measurements. It has previously been shown[5] that close to the 1:1 composition in the KCl–AlCl$_3$ system (from 47 to about 52 mol % KCl), the potential of the concentration cell used is, within the experimental uncertainty, given by eq 4, where pCl$^-_{\rm I}$ and pCl$^-_{\rm II}$ are the negative logarithms of the chloride concentrations in cell compartments I and II, respectively.

$$pCl^-_{\rm I} = -(F/(RT \ln 10))\Delta E + pCl^-_{\rm II} \qquad (4)$$

From the measured pCl$^-$ of the melt and from the formality of Fe(III), $\bar{n}$, the average experimental coordination number, can be calculated.

The spectra obtained were treated by a linear least-squares method developed especially for our spectral work.[4,5,10] Similar methods are known from the literature.[11,12] The method used is based on the Bouguer–Beer law and the law of additive absorbances expressed as a general equation involving three matrices (eq 5), where $l_m$ is the path length at the $m$th composition, $c_{mi}$ is the concentration of the $i$th species for the $m$th composition, $\epsilon_i(\nu_n')$ is the molar absorptivity of the $i$th species at the wavenumber $\nu_n'$, and $A_m(\nu_n')$ is the total absorbance of the $m$th composition at the wavenumber $\nu_n'$.

$$[l_m c_{mi}][\epsilon_i(\nu_n')] = [A_m(\nu_n')] \qquad (5)$$

An evaluation of the complexes of Fe(III) formed is based on the following method. As discussed in the Introduction (and as we shall see later), at low pCl$^-$ the only Fe(III) complex present is $FeCl_4^-$, which, therefore, is the natural starting point for the evaluation of the complex formation. Since the average experimental coordination number, $\bar{n}$, decreases with increasing pCl$^-$, chloride ions are taken away from $FeCl_4^-$ as the pCl$^-$ increases. This can be described in the model expressed in eq 6–9, where $v_i$, $x_i$, $y_i$, and $z_i$ are all integers. From the model

$$v_1FeCl_4^- \rightleftarrows Fe_{v_1}Cl_{z_1}{}^{3v_1-z_1} + (4v_1 - z_1)Cl^- \qquad (6)$$

$$v_2Fe_{v_1}Cl_{z_1}{}^{3v_1-z_1} \rightleftarrows x_2Fe_{y_2}Cl_{z_2}{}^{3y_2-z_2} + (z_1v_2 - x_2z_2)Cl^- \qquad (7)$$

$$v_3Fe_{y_2}Cl_{z_2}{}^{3y_2-z_2} \rightleftarrows x_3Fe_{y_3}Cl_{z_3}{}^{3y_3-z_3} + (z_2v_3 - x_3z_3)Cl^- \qquad (8)$$

$$\vdots$$

$$v_iFe_{y_{i-1}}Cl_{z_{i-1}}{}^{3y_{i-1}-z_{i-1}} \rightleftarrows x_iFe_{y_i}Cl_{z_i}{}^{3y_i-z_i} + (z_{i-1}v_i - x_iz_i)Cl^- \qquad (9)$$

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**Table I.** Values of Mole Fractions and Cell Potentials for 0.3 F $FeCl_3$ in Molten KCl–$AlCl_3$ at 300 °C

| mole fraction | | formality of $FeCl_3$ | $-\Delta E$, mV |
|---|---|---|---|
| KCl | $AlCl_3$ | | |
| $0.5091_2$ | $0.4709_2$ | 0.3049 | 32.42 |
| $0.5051_9$ | $0.4746_8$ | 0.3064 | 60.49 |
| $0.5034_7$ | $0.4773_9$ | 0.2910 | 81.47 |
| $0.5002_4$ | $0.4789_8$ | 0.3152 | 205.49 |
| $0.4966_9$ | $0.4833_9$ | 0.3026 | 530.4 |
| $0.4951_3$ | $0.4838_8$ | 0.3171 | 548.9 |
| $0.4926_0$ | $0.4872_3$ | 0.3041 | 571.5 |
| $0.4898_0$ | $0.4899_2$ | 0.3051 | 589.1[a] |
| $0.4897_6$ | $0.4898_5$ | 0.3068 | 589.1 |
| $0.4874_3$ | $0.4928_1$ | 0.2967 | 599.8 |
| $0.4845_1$ | $0.4956_2$ | 0.2977 | 612.2 |
| $0.4820_0$ | $0.4975_4$ | 0.3059 | 621.1 |
| $0.4797_4$ | $0.5002_0$ | 0.2994 | 625.1 |
| $0.4769_8$ | $0.5026_8$ | 0.3029 | $632.8_5$ |
| $0.4709_7$ | $0.5089_5$ | 0.2977 | $645.1_5$ |
| $0.4641_3$ | $0.5160_7$ | 0.2918 | $656.6_5$ |

[a] Measured with an open connection between the two cell chambers; the other measurements were made with a sealed connection.

put forward to explain the changes of the melt (for example, eq 6 and 7) and from arbitrarily chosen equilibrium constants, the concentration of each species can be calculated. Either these concentrations can be used to calculate a new $\bar{n}$ value or they can be introduced in matrix equation 5 (which now can be solved and for which the total absorptivities at all wavenumbers and compositions can be calculated). The best values of the equilibrium constants (i.e., giving the minimum deviations in both cases between measured and calculated values) can then be found by systematic variation of the equilibrium constants. Furthermore, by looking at different models, the minimum variance for each model can be obtained in this way. The ratio between the so obtained minimum variances and the lowest minimum variances (since an experimental variance could not be obtained in the present case) is then compared. On the basis of an *F* test, the distinction was made between models with more or less probability than 90%. Models with higher than 90% probability are marked with an asterisk in the tables.

To obtain $F_\alpha(\phi_N,\phi_D)$ (where $(1 - \alpha) \times 100\%$ is the probability and $\phi_N$ and $\phi_D$ are the numbers of degrees of freedom in the numerator and denominator, respectively) in connection with the potentiometric method, it was assumed that $\phi_N$ and $\phi_D$ were equal to the number of melt compositions minus the number of equilibrium constants in the calculations. In connection with the spectral measurements, $\phi_N$ and $\phi_D$ were assumed to be equal to the number of different melt compositions minus the number of species (with absorption in the measured range) minus, as before, the number of equilibrium constants involved in the calculations. In this case it was furthermore taken into consideration that part of the found minimum variance was due to noise in the measured spectra. By recording one of the spectra twice (each spectrum consists of 211 measured points), it was found that the variance due to noise ($v_{obsd}$) was ca. $3.9 \times 10^{-5}$. This value was subtracted from the minimum variance before the *F* test was made. However, the minimum variances given in this work are with noise included.

## Results and Discussion

**Potentiometric Measurements on 0.3 F $FeCl_3$ in KCl–$AlCl_3$ at 300 °C.** In Table I are given the values for mole fraction, formalities, and cell potential for 0.3 F $FeCl_3$ in KCl–$AlCl_3$ at 300 °C. The average experimental coordination number, $\bar{n}$, can be calculated from these data using the self-dissociation constants found for the solvent and discussed under General Considerations. A plot of $\bar{n}$ vs. $pCl^-$ is given in Figure 1. An examination of Figure 1 indicates that in the $pCl^-$ range from 0.6 to about 4 only one species is present, namely, $FeCl_4^-$. This is in agreement with our discussion in the Introduction and under the General Considerations. As we shall see later, the spectrum of the found species is in good agreement with the spectrum of the tetrachloroiron(III) complex in other media. It is also clear that as the $pCl^-$ is increased, $\bar{n}$ decreases indicating the formation of one or several iron species with lower average experimental coordination number than 4 as discussed under the General Considerations.

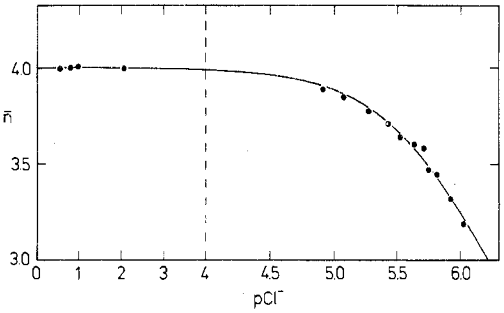

**Figure 1.** Average experimental coordination number for 0.3 F $FeCl_3$ in KCl–$AlCl_3$ at 300 °C as a function of $pCl^-$. The full line is calculated for the reactions $FeCl_4^- \rightleftarrows FeCl_3 + Cl^-$ (p*K* = 5.91) and $FeCl_3 \rightleftarrows FeCl_2^+ + Cl^-$ (p*K* = 6.53). The half-filled circle represents a coincidence between two filled circles.

**Table II.** Minimum Variances ($\times 10^4$)[a] Based on Potentiometric Measurements for Models[b] for 0.3 F $FeCl_3$ in KCl–$AlCl_3$ at 300 °C

| | $Fe_{v_1}Cl_{z_1}^{3v_1-z_1}$ | | | | | |
|---|---|---|---|---|---|---|
| $Fe_{y_2}Cl_{z_2}^{3y_2-z_2}$ | $Fe_2Cl_7^-$ | $FeCl_3$ | $Fe_2Cl_6$ | $Fe_2Cl_5^+$ | $FeCl_2^+$ | $Fe_2Cl_4^{2+}$ |
| no complex | *c* | 38.0 | 29.8 | 199 | 197 | 529 |
| $FeCl_3$ | 45.5 | | | | | |
| $Fe_2Cl_6$ | 28.7 | 27.1 | | | | |
| $Fe_2Cl_5^+$ | 6.4* | 8.4* | 29.9 | | | |
| $FeCl_2^+$ | 61.0 | 7.5* | 29.2 | 600 | | |
| $Fe_2Cl_4^{2+}$ | 30.9 | 4.6* | 26.0 | 218 | 218 | |

[a] Number of measurements = 16; asterisks based on $F_{0,10}(14.14) = 2.02$. [b] Given generally by $v_1 FeCl_4^- \rightleftarrows Fe_{v_1}Cl_{z_1}^{3v_1-z_1} + (4v_1 - z_1)Cl^-$ and $v_2 Fe_{v_1}Cl_{z_1}^{3v_1-z_1} \rightleftarrows x_2 Fe_{y_2}Cl_{z_2}^{3y_2-z_2} + (z_1v_2 - x_2z_2)Cl^-$. [c] There is no reason to make a calculation here, since $\bar{n}$ cannot be lower than 3.5 for this model.

In the KCl–$FeCl_3$ system where the concentration of Fe(III) was more than 20 times higher than in the present case, no complex containing more than two iron atoms was found. It is therefore reasonable to assume that there are no more than two iron atoms linked together in any species in the dilute system. This will, of course, reduce the number of possible equilibria to be considered. Furthermore, the models are limited by the assumption that $\bar{n} \geq 2$. This assumption is reasonable since the lowest $\bar{n}$ found is 3.18. On the basis of eq 6 and 7, all of the possible models which can be taken into account are given in Table II together with the obtained minimum variances. The $\bar{n}$ values shown in Figure 1 for $pCl^-$ values below 4.0 are not used in these calculations because they give no information concerning the complexes other than an indication of the existence of $FeCl_4^-$. The values can, however, be used to calculate the experimental variance for $pCl^- < 4$ (a calculation yields a variance of $1.7 \times 10^{-5}$), but this variance is not constant for the whole $pCl^-$ range. As can be seen from Figure 1, the uncertainty is higher at higher $pCl^-$ values. Therefore an *F* test cannot be performed using the experimental variance; instead we have to use the next best method of assuming that the lowest obtained minimum variance is the same as the experimental variance for the examined $pCl^-$ range. If this method is used, the four models marked with

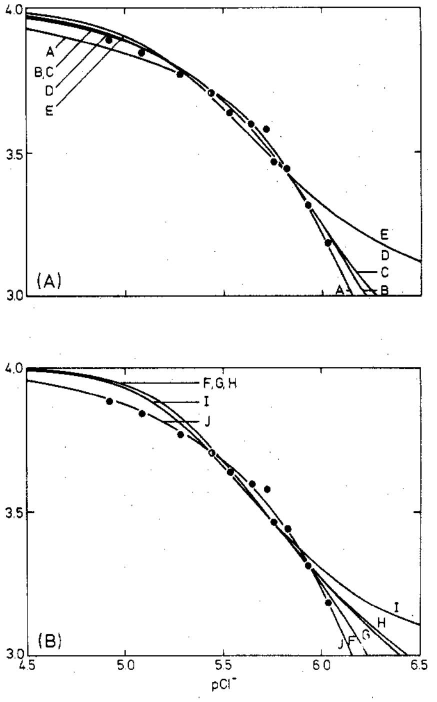

**Figure 2.** Average experimental coordination number (filled circles) for 0.3 F $FeCl_3$ as a function of $pCl^-$ in $KCl-AlCl_3$ at 300 °C compared with calculated values (full lines) for a series of reaction schemes, which were in reasonably good agreement with the experimental data. Fe(III) species in equilibrium with $FeCl_4^-$ and $Cl^-$: A, $Fe_2Cl_7^-$, $Fe_2Cl_5^+$; B, $FeCl_3$, $FeCl_2^+$; C, $FeCl_3$, $Fe_2Cl_5^+$; D, $FeCl_3$, $Fe_2Cl_6$; E, $Fe_2Cl_7^-$, $Fe_2Cl_6$; F, $Fe_2Cl_6$, $Fe_2Cl_4^{2+}$; G, $Fe_2Cl_6$, $FeCl_2^+$; H, $Fe_2Cl_6$, $Fe_2Cl_5^+$; I, $Fe_2Cl_6$; J, $FeCl_3$, $Fe_2Cl_4^{2+}$. The half-filled circle represents a coincidence between two filled circles.

**Table III.** Comparison between the Four Best Models for 0.3 F $FeCl_3$ in $KCl-AlCl_3$ at 300 °C Based on Potentiometric Measurements

| equilibria | model no. | p*K* | 95% confidence limits |
|---|---|---|---|
| $2FeCl_4^- \rightleftarrows Fe_2Cl_7^- + Cl^-$ | 1 | 4.97 | 4.87-5.06 |
| $Fe_2Cl_7^- \rightleftarrows Fe_2Cl_5^+ + 2Cl^-$ | | 11.95 | 11.88-12.02 |
| $FeCl_4^- \rightleftarrows FeCl_3 + Cl^-$ | 2 | 5.88 | 5.84-5.92 |
| $2FeCl_3 \rightleftarrows Fe_2Cl_5^+ + Cl^-$ | | 5.80 | 5.66-5.98 |
| $FeCl_4^- \rightleftarrows FeCl_3 + Cl^-$ | 3 | 5.91 | 5.87-5.95 |
| $FeCl_3 \rightleftarrows FeCl_2^+ + Cl^-$ | | 6.53 | 6.43-6.65 |
| $FeCl_4^- \rightleftarrows FeCl_3 + Cl^-$ | 4 | 5.83 | 5.80-5.86 |
| $2FeCl_3 \rightleftarrows Fe_2Cl_4^{2+} + 2Cl^-$ | | 12.11 | 11.99-12.26 |

asterisks in Table II are possible models clearly distinguishable from the other models (i.e., with considerably lower variance).

It would now be of interest to look in more detail at some of the models given in Table II, and this is done in Figure 2. Here eight of the models with the lowest variances are used for comparison of the obtained $\bar{n}$ values at different $pCl^-$ values. From this figure it can be seen that models A, B, C, and J are in better agreement with the experimental values than are the other models. This is the same result as is indicated by Table II. Finally, it is interesting to compare the values for the equilibrium constants (given as p*K* values) for the four possible models given in Table II. These values are given in Table III. It is noteworthy that the first equilibrium for the last three models (models 2, 3, and 4) in Table III are the same and that the p*K* values for this equilibrium are almost independent of the second equilibrium. The next step in the examination of the iron complexes is to examine the spectra of the melts.

**Spectrophotometric Measurements on 0.3 F $FeCl_3$ in $KCl-AlCl_3$ at 300 °C.** The spectrophotometric measurements have been performed on a series of $KCl-AlCl_3$ melts with a formality of $FeCl_3$ close to 0.3 F. Some of these spectra are shown in Figure 3. It is, as discussed under the General Considerations, possible from such a set of spectra to calculate the equilibrium constants and minimum variances for a number of different models. In Table IV are given the calculated minimum variances for the same models as treated in connection with the potentiometric measurements (see Table II). It should be noted here that the variances have only been examined within the 95% confidence limits calculated for the p*K* values examined by the potentiometric method. In Table IV it can be seen that eight models have to be considered based on the spectrophotometric method. However, from a comparison of Table II and Table IV it is clear that there now are only three possibilities left (the last three models in Table III). Since the spectra of all of the iron species are rather similar and have broad bands, it is not possible to obtain accurate equilibrium constants from the spectrophotometric measurements and they are, therefore, not given in a table. Spectrophotometrically and potentiometrically there is no way to distinguish between the last three models in Table III. The important thing, however, is that only one of the three models has mononuclear Fe(III) complexes, and the low total Fe(III) concentration makes dimeric species rather unlikely. Model 3 in Table III is therefore the most likely model with the species $FeCl_4^-$, $FeCl_3$, and $FeCl_2^+$. It is important also to note

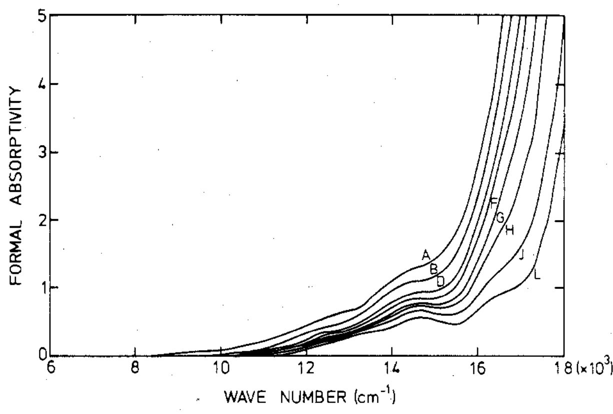

**Figure 3.** Series of spectra of 0.3 F $FeCl_3$ in $KCl-AlCl_3$ at 300 °C. Mole fractions of KCl and $AlCl_3$, respectively: A, $0.4728_6$, $0.5070_7$; B, $0.4770_5$, $0.5030_4$; C, $0.4804_0$, $0.4998_2$; D, $0.4818_6$, $0.4981_6$; E, $0.4840_3$, $0.4963_3$; F, $0.4861_4$, $0.4937_0$; G, $0.4902_1$, $0.4894_6$; H, $0.4939_6$, $0.4865_2$; I, $0.4977_0$, $0.4831_8$; J, $0.4978_2$, $0.4828_1$; K, $0.4999_2$, $0.4807_9$; L, $0.5018_5$, $0.4789_4$; M, $0.5019_2$, $0.4791_1$. For reasons of clarity some of the recorded spectra are not shown in this figure (but are used in the calculations).

**Table IV.** Minimum Variances (× 10⁵)[a] Based on Spectrophotometric Measurements for Models[b] for 0.3 F $FeCl_3$ in $KCl-AlCl_3$ at 300 °C

| | $Fe_{v_1}Cl_{z_1}{}^{3v_1-z_1}$ | | | | | |
|---|---|---|---|---|---|---|
| $Fe_{y_2}Cl_{z_2}{}^{3y_2-z_2}$ | $Fe_2Cl_7^-$ | $FeCl_3$ | $Fe_2Cl_6$ | $Fe_2Cl_5^+$ | $FeCl_2^+$ | $Fe_2Cl_4^{2+}$ |
| no complex | *c* | 46 | 28.5 | 108 | 112 | 303 |
| $FeCl_3$ | 248 | | | | | |
| $Fe_2Cl_6$ | 22.2 | 15.3* | | | | |
| $Fe_2Cl_5^+$ | 18.9 | 9.1* | 19.6 | | | |
| $FeCl_2^+$ | 11.3* | 9.3* | 18.6 | 14.5* | | |
| $Fe_2Cl_4^{2+}$ | 55.6 | 8.7* | 15.0* | 11.1* | 24.7 | |

[a] Calculated within the 95% confidence limits found by potentiometric measurement; number of spectra = 13; number of different wavenumbers = 211; wavenumber range = 11.1 × 10³–17.7 × 10³ cm⁻¹; asterisks based on $F_{0.10}(8.8) = 2.59$ and $v_{obsd} = 3.9 \times 10^{-5}$. [b] Given generally by: $v_1FeCl_4^- \rightleftarrows Fe_{v_1}Cl_{z_1}{}^{3v_1-z_1} + (4v_1 - z_1)Cl^-$ and $v_2Fe_{v_1}Cl_{z_1}{}^{3v_1-z_2} \rightleftarrows x_2Fe_{y_2}Cl_{z_2}{}^{3y_2-z_2} + (z_1v_2 - x_2z_2)Cl^-$. [c] There is no reason to make a calculation here, since $\bar{n}$ cannot be lower than 3.5 for this model.

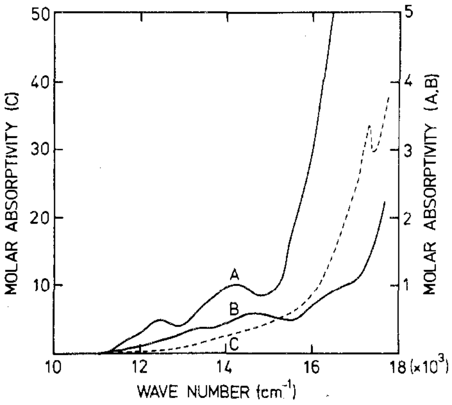

**Figure 4.** Calculated spectra for 0.3 F $FeCl_3$ in KCl–$AlCl_3$ at 300 °C: A, $FeCl_4^-$; B, $FeAlCl_7^-$; C, $FeAlCl_6$. Each spectrum is calculated from 13 measured spectra based on $FeCl_4^- + AlCl_4^- \rightleftarrows FeAlCl_7^- + Cl^-$ (p$K$ = 6.75) and $FeAlCl_7^- \rightleftarrows FeAlCl_6 + Cl^-$ (p$K$ = 6.53) and the equilibrium constants for KCl–$AlCl_3$ (see text). The dashed line indicates a greater uncertainty for the calculated spectrum of $FeAlCl_6$ than for the other spectra.

that the solvation has not been taken into consideration until this point. It is, for example, extremely unlikely that $FeCl_3$ is present in the melt as such. This particular problem has been discussed previously in connection with the KCl–$FeCl_3$ system.[4] The spectra of $FeCl_3$ and $FeCl_2^+$ are (as will be shown later) rather similar to the spectra of well-known tetrahedrally bound Fe(III) complexes such as $FeCl_4^-$ and $Fe_2Cl_6$. It is therefore most likely that we are dealing with tetrahedrally bound Fe(III) in this case also. It should, however, be mentioned that it is not easy to interpret spectra of Fe(III). Possible complexes could be $[FeCl_3(AlCl_4)]^-$, $[FeCl_2(AlCl_4)_2]^-$, or $[FeCl_2(AlCl_4)]$. It should be noted that these complexes can be obtained by exchanging one aluminum atom with one iron atom in $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, and $Al_2Cl_6$, respectively. A comparison with the pure KCl–$AlCl_3$ and KCl–$FeCl_3$ systems suggests—if exchange of Al(III) atoms with Fe(III) atoms is assumed—that the most likely equilibria in the melt are those of eq 10 and 11, with equilibrium

$$FeCl_4^- + AlCl_4^- \rightleftarrows AlFeCl_7^- + Cl^- \qquad (10)$$

$$AlFeCl_7^- \rightleftarrows AlFeCl_6 + Cl^- \qquad (11)$$

constants $K_1$ and $K_2$, respectively. Since the concentration of $AlCl_4^-$ in the melt is known and nearly constant, the p$K$ value for eq 10 can easily be calculated (from Table III) to be 6.75 ± 0.03. The equilibrium constant for eq 11 will, of course, be the same as in Table III (i.e., with 95% confidence limits 6.43–6.65 or with a standard error of 6.53 ± 0.06).

As discussed under the General Considerations, it is possible to calculate the spectrum of each species for any particular model. The resulting spectra of $FeCl_4^-$, $AlFeCl_7^-$, and $AlFeCl_6$ are given in Figure 4. The sharp peak at 17.3 × $10^3$ cm$^{-1}$ in the spectrum of $AlFeCl_6$ is probably spurious. This is due to the concentration of $AlFeCl_6$ being small, and hence the calculation of the spectrum is uncertain. The uncertainties in the spectra are, for convenience, divided into two parts. The main part arises from the uncertainties in the equilibrium constants (which have been varied within their 95% confidence limits). A smaller part is due to the process of separating the measured spectra into those for the single species. Altogether, the average uncertainties in the molar extinction coefficients for the given spectra are approximately ±1, ±5, and ±20% for $FeCl_4^-$, $AlFeCl_7^-$, and $AlFeCl_6$, respectively. It is, of course also interesting to compare the spectrum of $FeCl_4^-$ obtained here with other known spectra of $FeCl_4^-$. This is done in Figure 5. Here the spectrum of $FeCl_4^-$ in KCl–$AlCl_3$ is compared with the spectrum of $FeCl_4^-$ in KCl–$FeCl_3$. It is obvious that the spectra are very similar. But it is also clear that there is some resemblance to the spectrum obtained by Balt[2] in acetone at 25 °C.

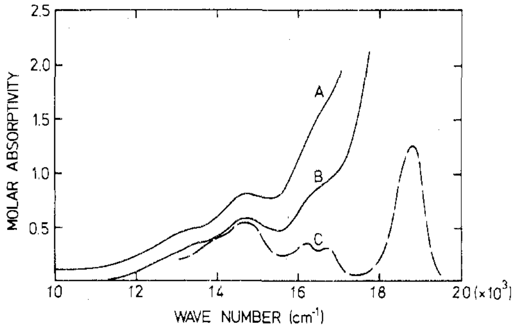

**Figure 5.** Comparison between calculated and measured spectra of $FeCl_4^-$: A, in KCl–$FeCl_3$ at 300 °C (calculated, see ref 4); B, in KCl–$AlCl_3$ at 300 °C (calculated); C, in acetone (as tetraethylammonium tetrachloroferrate) at 25 °C measured by Balt.[2]

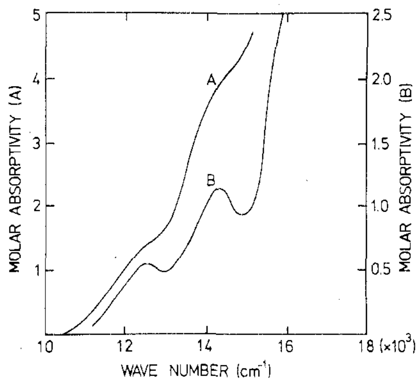

**Figure 6.** Comparison between the calculated spectrum of $Fe_2Cl_7^-$ (A) in KCl–$FeCl_3$ at 300 °C (see ref 4) and the calculated spectrum of $FeAlCl_7^-$ (B) in KCl–$AlCl_3$ at 300 °C. Note that two different absorptivity scales have been used in order to compare the absorptivities due to the Fe(III) chromophores.

In Figure 6 another interesting comparison is made. Here the spectrum of $FeAlCl_7^-$ in KCl–$AlCl_3$ calculated from the present measurements is compared with the spectrum of $Fe_2Cl_7^-$ in KCl–$FeCl_3$ obtained previously.[4] It should be noted that two different absorptivity scales have been used in order to compare the absorptivity due to the Fe(III) chromophore. From this figure it is clear that there is a close resemblance between the spectra of the two complexes.

Very interesting is the value for the equilibrium constants for exchange reactions 12 and 13. Since the aluminum and

$$Al_2Cl_7^- + Fe_2Cl_7^- \rightleftarrows 2AlFeCl_7^- \qquad (12)$$

$$Al_2Cl_6 + Fe_2Cl_6 \rightleftarrows 2AlFeCl_6 \qquad (13)$$

iron complexes are rather similar with respect to Lewis acid acidity, it is logical to see if there is a simple statistical distribution between iron and aluminum atoms. This will give us equilibrium constants of 4 for both reactions (i.e., p$K$ values of −0.60). In order to calculate the equilibrium constants for these reactions it is necessary to assume that there is no change in activity coefficients in going from KCl–$AlCl_3$ to KCl–$FeCl_3$. This assumption will be discussed later. The p$K$ values for reactions 12 and 13 were based on this assumption and were found to be −0.65 ± 0.06 and 0.2 ± 0.2, respectively. It can therefore be seen that the distribution for reaction 12 is almost statistical, whereas the distributions for reaction 13 favor the formation of homonuclear complexes. The equilibrium constant for this latter reaction is rather similar to the constant found in the gaseous phase where a p$K$ value of −0.2 has been obtained by Shieh and Gregory.[13] Some additional measurements will be given here.

**Table V.** Values of Mole Fractions and Cell Potentials[a] for 0.3 F AlCl$_3$ in Molten KCl-FeCl$_3$ at 300 °C

| mole fraction | | formality of AlCl$_3$ | $-\Delta E$, mV |
|---|---|---|---|
| KCl | FeCl$_3$ | | |
| $0.5003_7$ | $0.4817_7$ | 0.2817 | 188.03 |
| $0.4867_5$ | $0.4941_1$ | 0.2989 | 457.0 |
| $0.4785_9$ | $0.5018_7$ | 0.3031 | 481.8 |
| $0.4671_9$ | $0.5137_5$ | 0.2934 | 504.9 |

[a] Measured with sealed connection between cell chambers.

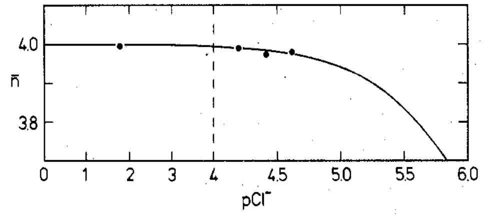

**Figure 7.** Average experimental coordination number for 0.3 F AlCl$_3$ in KCl–FeCl$_3$ at 300 °C as a function of pCl$^-$. The full line is calculated for the reaction AlCl$_4^-$ ⇄ AlCl$_3$ + Cl$^-$ (p$K$ = 6.2).

**Potentiometric Measurements on 0.3 F AlCl$_3$ in KCl–FeCl$_3$ at 300 °C.** A consequence of the given model (i.e., eq 1, 2, 10, and 11) is that for the reversed system (AlCl$_3$ in KCl–FeCl$_3$) one would expect AlCl$_4^-$, FeCl$_4^-$, Fe$_2$Cl$_7^-$, Fe$_2$Cl$_6$, and FeAlCl$_7^-$, and perhaps FeAlCl$_6$, to be present. In order to prove this we performed a series of measurements on 0.3 F AlCl$_3$ in KCl–FeCl$_3$. The values of mole fractions, formalities, and potentials are given in Table V. The calculated values for $\bar{n}$ vs. pCl$^-$ are given in Figure 7. Unfortunately, it is not possible to obtain much higher pCl$^-$ values than shown on this figure. This is due to the fact that FeCl$_3$ is not as strong a Lewis acid as AlCl$_3$. Therefore, only one equilibrium (where solvation has not been taken into consideration), eq 14, has

$$\mathrm{AlCl_4^-} \rightleftarrows \mathrm{AlCl_3} + \mathrm{Cl^-} \qquad (14)$$

been considered in order to obtain agreement between measurements and calculation. The p$K$ value for this reaction is found to be in the range 5.8–6.6 (95% confidence limits). The curved line in Figure 7 is calculated for p$K$ = 6.2. The variance for this model (with p$K$ = 6.2) is $5.1 \times 10^{-5}$ in good agreement with what can be expected. On the basis of the p$K$ value for eq 14, we can calculate a p$K$ value for eq 10 of 6.6–7.4 (95% confidence limits). The last value compares favorably with the value of 6.75 ± 0.03 found for 0.3 F FeCl$_3$ in KCl–AlCl$_3$. This result is, therefore, in good agreement with the concept of no change in activity coefficients in mixtures from KCl–AlCl$_3$ to KCl–FeCl$_3$. This is also very reasonable considering all of the other similarities between KCl–AlCl$_3$ and KCl–FeCl$_3$. The same molar volumes are, for example, found in both systems at comparable melt compositions and temperatures indicating that complexes with the same size are formed in the two systems. Another way to check the proposed model for the iron system would be to look at gas-phase spectra of Fe$_2$Cl$_6$ and mixtures of Fe$_2$Cl$_6$ and Al$_2$Cl$_6$.

**Gas-Phase Spectra of Fe$_2$Cl$_6$ and Mixtures of Fe$_2$Cl$_6$ and Al$_2$Cl$_6$.** As mentioned above, the p$K$ value for eq 13 in the gaseous phase was found by Shieh and Gregory[13] and agreed well with the value found in the KCl–AlCl$_3$ melt. However, the spectra obtained by Shieh and Gregory were not measured in the wavenumber range of interest for us. The present absorption spectra are based on measurements on saturated vapors of Fe$_2$Cl$_6$ at 300 °C, and furthermore on saturated vapors of Fe$_2$Cl$_6$ with 0.0348 M AlCl$_3$ added, also at 300 °C. This addition increased the absorbance at all measured wavenumbers (from 10.0 to $22.2 \times 10^3$ cm$^{-1}$). Since Al$_2$Cl$_6$ does not absorb in this range, there must be a mixed complex formed. From these measurements and from the vapor-pressure measurements by Johnstone et al.[14] and the equilibrium constants for eq 13 by Shieh and and Gregory,[13] the spectra of Fe$_2$Cl$_6$ and AlFeCl$_6$ were calculated as shown in Figure 8. Finally, it is appropriate to compare the spectrum of FeAlCl$_6$ in the gaseous phase with the FeAlCl$_6$ spectrum calculated from the measurements on 0.3 F FeCl$_3$ in KCl–AlCl$_3$ at 300 °C. This is done in Figure 9. As it can be seen, there is a rather good agreement between the two types of spectra. The sharp band at $17.3 \times 10^3$ cm$^{-1}$ is, as mentioned above, probably spurious.

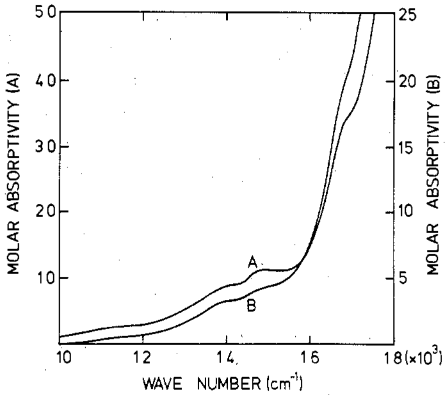

**Figure 8.** Gas-phase Fe(III) complexes: A, Fe$_2$Cl$_6$; B, FeAlCl$_6$. Note that two different absorptivity scales have been used in order to compare the absorptivities due to Fe(III).

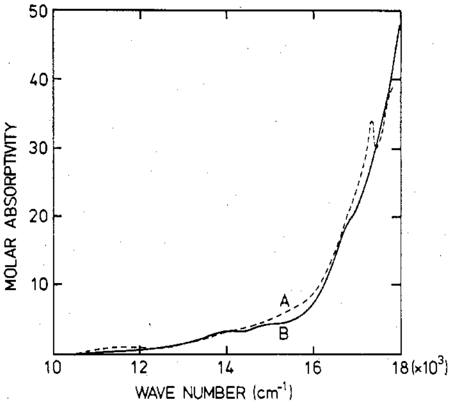

**Figure 9.** Comparison between the calculated and measured spectrum of FeAlCl$_6$: A, in KCl–AlCl$_3$ at 300 °C (calculated); B, in the gaseous phase (measured).

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**Registry No.** AlCl$_4^-$, 17611-22-2; FeCl$_4^-$, 14946-92-0; FeAlCl$_7^-$, 67951-74-0; FeAlCl$_6$, 55399-03-6; Al$_2$Cl$_6$, 13845-12-0; Fe$_2$Cl$_6$, 16480-60-7.

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