On Extraction with Long Chain Tertiary Amines

X. The Mechanism of the Extraction of Trivalent Iron by Trilauryl-ammonium Chloride

LIBOR KUČA* and ERIK HÖGFELDT

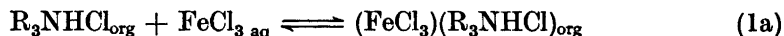*Royal Institute of Technology (KTH), Stockholm 70, Sweden*

The distribution of Fe(III) between solutions of trilaurylammonium chloride (BHCl) in *o*-xylene and aqueous 1 M (Fe(III), 0.1 M H, Li)Cl has been studied by the two-phase titration technique. The equilibrium concentration of Fe(III) in the aqueous phase has been determined by emf measurements of the Fe^{3+}/Fe^{2+} couple. The concentration ranges used were for [BHCl] 0.01 M — 0.30 M, for $[Fe(III)]_{aq}$ 2×10^{-5} M — 2×10^{-2} M. The experimental data were fitted to three mechanisms, using $(FeCl_3)p(BHCl)q$ as a general formula of the extracted complex:

    I. Complexes (p,q) of small size, no aggregation of BHCl
    II. Complexes (p,q) of small size, BHCl aggregated
    III. The size of (p,q) complexes comparable with the size of BHCl aggregates.

    Calculations were performed on mechanism III only in the range 0.01 — 0.1 M $[BHCl]_{org}$. While mechanism II seems to be ruled out, I and III give practically the same fit. However, III is the only one possible when considering the aggregation equilibria found in the system (*cf.* Ref 1). The relevant equilibrium constants and their standard deviations are given in Table 2. The reason that mechanism I is a good way of describing the iron extraction may be due to the fact that the Fe—Cl complexes are formed practically independently of whether the chloride ions belong to monomers or aggregates.

The system Fe(III)-HCl-trilaurylammonium chloride (R_3NHCl) has been widely studied from different points of view, but a consistent description of the system is lacking at present. Investigations carried out by different techniques, *e.g.* by two-phase titration (Högfeldt and Tavares[1]) or by osmometry (*e.g.* Müller and Diamond[2]) have established a considerable aggregation of R_3NHCl in organic solvents of low dielectric constant. The results of the distribution studies of iron in tracer concentrations seem to be fairly well explained by the following equilibria[3]

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* Present address: Institute of Nuclear Research, Řež near Prague, Czechoslovakia.

$$R_3NHCl_{org} + FeCl_{3\ aq} \rightleftharpoons (FeCl_3)(R_3NHCl)_{org} \qquad (1a)$$

$$(FeCl_3)(R_3NHCl) + R_3NHCl \rightleftharpoons (FeCl_3)(R_3NHCl)_2 \qquad (1b)$$
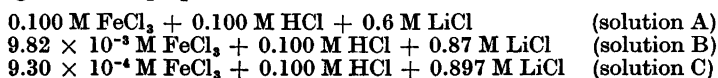
where the position of the second equilibrium is determined solely by the dielectric nature of the diluent, neglecting the aggregation of R_3NHCl. Thus in solvents of high dielectric constant (*e.g.* in nitrobenzene, where the aggregation of R_3NHCl can be assumed to be negligible, see Nelson *et al.*[3]) reaction (1b) lies to the left with the main iron-R_3NHCl species (1,1) and in low dielectric solvents (*e.g.* White *et al.*[4], Müller *et al.*[5]) the complex found has the composition (1,2). With macroconcentrations of iron, even in the low dielectric solvent, toluene, Duyckaerts *et al.*[6] have found (1,2) as well as the (1,1) complex.

In the present work the system trilaurylammonium chloride-*o*-xylene-0.1 M HCl, 1.0 M (Fe(III), H^+, Li^+)Cl, in which the extent of the aggregation of R_3NHCl was established by Högfeldt and Tavares,[1] was chosen.*
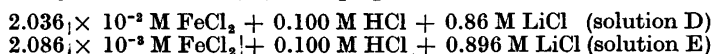
EXPERIMENTAL

Chemicals. Trilaurylamine (B, tridodecylamine) from Rhône-Poulenc with 1 % of primary and secondary amines, *o*-xylene (Kebo, Stockholm) with 98—100 % purity, lithium chloride (Mallinckrodt, A. R.), hydrochloric acid *p.a.*, iron(III) chloride *p.a.* and iron(II) chloride *p.a.* (all Merck) were used without further purification.

Solutions. The extractions were performed with solutions of BHCl in *o*-xylene and aqueous phases of constant ionic medium (1.0 M Cl^-) and constant acidity (0.1 M H^+). A weighed amount of B dissolved in *o*-xylene was shaken for 5 h with an aqueous solution containing 0.9 M LiCl and the calculated amount of HCl necessary to convert B to BHCl and leave the equilibrium aqueous phase 0.1 M in HCl. According to Högfeldt and Tavares [1] all of B at equilibrium with 0.1 M HCl, 0.9 M LiCl is in the form of the ammonium salt. The acidity of the equilibrium aqueous phase was checked by titration with standard 0.1 M NaOH. From a stock solution of 0.290 M $FeCl_3$, 0.0966 M HCl were the following solutions prepared:

> 0.100 M $FeCl_3$ + 0.100 M HCl + 0.6 M LiCl   (solution A)
> 9.82×10^{-3} M $FeCl_3$ + 0.100 M HCl + 0.87 M LiCl   (solution B)
> 9.30×10^{-4} M $FeCl_3$ + 0.100 M HCl + 0.897 M LiCl   (solution C)

The stock solution and the solution A have been standardised after reduction with $SnCl_2$ by titration with 0.03 M $K_2Cr_2O_7$,[7] and gravimetrically by precipitation with NH_3 and weighing as Fe_2O_3.[8] The concentration of Fe(III) in solutions B and C was determined by redox titration in the presence of Fe(II) with solution A or B, respectively, using the Gran extrapolation.[9]

The following solutions of Fe(II) were prepared:

> 2.036×10^{-2} M $FeCl_2$ + 0.100 M HCl + 0.86 M LiCl   (solution D)
> 2.086×10^{-3} M $FeCl_2$ + 0.100 M HCl + 0.896 M LiCl (solution E)

The concentration of total iron in solution D was determined again both by titration with $K_2Cr_2O_7$ and as Fe_2O_3. The concentration of iron in solution E has been calculated from the dilution. All solutions A through E as well as the BHCl solutions were saturated with nitrogen and kept in a nitrogen atmosphere.

Experimental technique. Two-phase titrations were performed in equipment similar to that given by Högfeldt and Fredlund.[10] The cell used for the emf measurement was

Ag, AgCl(s) | 0.1 M HCl, 0.9 M LiCl || 1.0 M (Fe(III), Fe(II), 0.1 M H^+, Li^+) Cl^- | Pt

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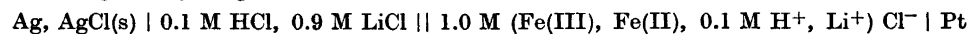
* A short summary of the content in this paper was presented at ICSEC in Göteborg, Aug. 27 to Sept. 1, 1966, *cf.* Proceedings, North Holland 1967, p. 454, by Kuča, Högfeldt and Sillén.

The emf was measured with a PHM4 valve potentiometer (Radiometer). The solution in the titration vessel was stirred with a mechanical stirrer and kept in an atmosphere of oxygen-free nitrogen. The experiments were performed in the following way. The solution of Fe(II) was brought into the vessel. After the potential on the Pt electrode reached a constant value, the solution was titrated with a Fe(III) solution. From this titration (by the use of a Gran diagram[9]) the concentration of Fe(III) present in the Fe(II) solution as well as $E°$ in eqn. (2) were determined.

$$E = E° + 59.156 \log ([Fe^{3+}]/[Fe^{2+}]) \tag{2}$$

The actual two-phase titration was performed in two ways. To the aqueous phase either the solution of BHCl in o-xylene was added from the buret or else only one portion of the BHCl solution was added and then titrated with Fe(III) solution.

After the two-phase titration was finished, the concentration of total iron in the aqueous phase was determined spectrophotometrically with 1,10-phenanthroline.[11]

Distribution of Fe(II). The extraction of Fe(II) by BHCl was measured using a tracer technique. [59]Fe tracer obtained as iron(II) ammonium sulfate from the Radiochemical Centre, Amersham, was oxidized with HNO_3, precipitated with NH_3 and dissolved in HCl. After evaporation solid $FeCl_3$ was obtained, which was dissolved in 0.1 M HCl, 0.9 M LiCl. Before each extraction iron(III) was reduced to iron(II) by metallic iron powder. To keep iron in the iron(II) state, platinum foil covered with platinum black was inserted and oxygen-free hydrogen was passed through the solution. Extraction was started with 0.047 M BHCl in o-xylene. Each hour samples were taken from both phases and their activities measured. After equilibrium was reached, portions of 0.31 M BHCl were added and the distribution ratios were determined in the same way.

The γ-activity measurements were carried out in a Tracerlab SC-57 well scintillation counter with a Tracerlab SC-70 Compu/Matic V Scaler at 1200 V and 0.25 V sensitivity.
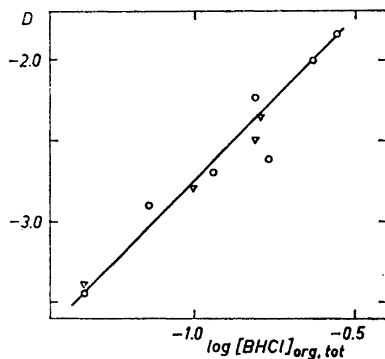

Fig. 1. Apparent distribution ratio of [59]Fe(II) between solutions of BHCl in o-xylene and 1.0 M (H^+, Li^+)Cl^- as a function of log $[BHCl]_{org, tot}$. Considering the possible oxidation of small amounts of Fe(II) to Fe(III) (see p. 186) the experimental points may not represent the distribution of Fe(II) only. The line is drawn with a slope 2. The symbols O, ▽ refer to two sets of experiments.
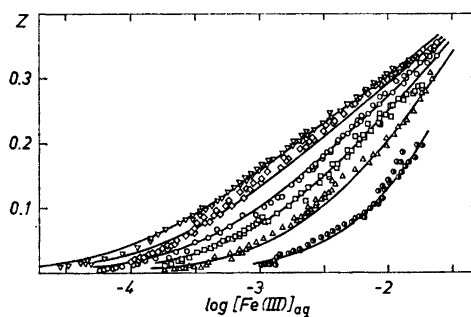
Fig. 2. Z as a function of log $[Fe(III)]_{aq}$ for various $[BHCl]_{org}$. ▽ 0.300 M BHCl, ◇ 0.220 M BHCl, O 0.150 M BHCl, □ 0.100 M BHCl, △ 0.050 M BHCl, ◐ 0.010 M BHCl.

RESULTS

Extraction of Fe(II). The experimental results of the distribution of Fe(II) are given in Fig. 1. The line drawn through the points has the slope 2, which could mean that the extraction of Fe(II) proceeds by the reaction

$$(FeCl_2)_{aq} + 2(BHCl)_{org} \rightleftharpoons (FeCl_2)(BHCl)_{2\,org} \tag{3}$$

On the other hand it has been found that — at least for the tracer concentrations — Fe(III) is extracted by a similar mechanism,[4,5] but to a greater extent. For 0.15 M BHCl the distribution ratios found are $D_{Fe(III)} = 19.1$ and $D_{Fe(II)} = 0.0044$. If about 0.01 % of Fe(II) was oxidized to the trivalent state, this would give rise to a distribution ratio of the same magnitude. As the concentration of Fe(II) was 0.011 M, the possible concentration of oxidized Fe is below the sensitivity of the thiocyanate method. The results given in Fig. 1 therefore should be considered with caution and they were used merely as an indication of the upper limit of the extraction of Fe(II), as will be discussed later.

Extraction of Fe(III). The two-phase titration measurements were performed for six concentrations of BHCl ranging from 0.01 M to 0.30 M. The experimental data are given in Table 1 and plotted in Fig. 2 as $Z = f(\log[Fe(III)]_{aq})$, where

$$Z = [Fe(III)]_{org}/[BHCl]_{org,\,tot} \tag{4}$$

Table 1. Corresponding values of $-\log[Fe(III)]aq$, Z.

$[BHCl]_{org} = 0.010$ M
1.729, 0.194; 1.768, 0.197; 1.795, 0.177; 1.827, 0.170; 1.859, 0.163; 1.886, 0.154; 1.911, 0.146;
1.883, 0.186; 1.927, 0.170; 1.964, 0.154; 2.000, 0.142; 2.035; 0.133; 2.071, 0.125;
1.904, 0.170; 1.948, 0.154; 1.985, 0.138; 2.020, 0.127; 2.044, 0.114; 2.069, 0.105;
2.060, 0.110; 2.104, 0.105; 2.145, 0.0989; 2.183, 0.0934; 2.222, 0.0886; 2.254, 0.831; 2.285, 0.0782;
2.184, 0.0842; 2.239, 0.0845; 2.288, 0.0767; 2.344, 0.0736; 2.392, 0.0682; 2.434, 0.0630; 2.473, 0.0584;
2.525, 0.0539; 2.576, 0.0488; 2.618, 0.0429; 2.692, 0.0356; 2.750, 0.0301; 2.679, 0.0341; 2.738, 0.0331; 2.784, 0.0287; 2.841, 0.0276; 2.863, 0.0233; 2.882, 0.0203; 2.890, 0.0176; 2.880, 0.0114; 2.922, 0.0118; 2.959, 0.0117; 2.992, 0.0113;
3.091, 0.00365; 3.130, 0.00519; 3.180, 0.00621; 3.221, 0.00622; 3.253, 0.00591;

$[BHCl]_{org} = 0.050$ M
1.647, 0.298; 1.700, 0.279; 1.743, 0.267; 1.788, 0.249; 1.848, 0.236; 1.924, 0.225; 2.011, 0.207;
1.656, 0.308; 1.730, 0.276; 1.800, 0.249; 1.881, 0.231; 1.950, 0.212; 2.019, 0.196; 2.084, 0.182; 2.144, 0.169;
2.106, 0.182; 2.190, 0.174; 2.265, 0.159; 2.346, 0.148; 2.408, 0.135; 2.461, 0.123; 2.511, 0.113; 2.560, 0.104; 2.601, 0.0967; 2.640, 0.0901; 2.675, 0.0843; 2.709, 0.0791;
2.429, 0.140; 2.490, 0.114; 2.561, 0.105; 2.618, 0.0944; 2.671, 0.0854; 2.760, 0.0712; 2.784, 0.0572; 2.924, 0.0426;
2.436, 0.127; 2.489, 0.121; 2.560, 0.111; 2.621, 0.100; 2.726, 0.0819; 2.822, 0.0700; 2.900, 0.0603; 2.969, 0.0530; 3.030, 0.0472; 3.076, 0.0423; 3.150, 0.0349; 3.160, 0.0291;
3.100, 0.0361; 3.128, 0.0325; 3.150, 0.0293; 3.233, 0.0299; 3.208, 0.0212; 3.349, 0.0244; 3.405, 0.0147; 3.469, 0.00713; 3.620, 0.00611;
3.414, 0.0116; 3.511, 0.00757; 3.572, 0.00554; 3.617, 0.00491; 3.656, 0.00512; 3.728, 0.00469; 3.559, 0.0115;

$[BHCl]_{org} = 0.100$ M
1.602, 0.294; 1.734, 0.285; 1.802, 0.276; 1.871, 0.266; 1.956, 0.258; 2.008, 0.243; 2.070,
0.231; 2.128, 0.219; 2.184, 0.208; 2.234, 0.197; 2.278, 0.187; 2.322, 0.178; 2.400, 0.162;
2.466, 0.148;
1.626, 0.326; 1.749, 0.287; 1.912, 0.267; 2.059, 0.238; 2.187, 0.211; 2.295, 0.187; 2.387,
0.167; 2.463, 0.150; 2.527, 0.137; 2.642, 0.110;
1.728, 0.288; 1.794, 0.279; 1.852, 0.275; 1.914, 0.268; 1.981, 0.257; 2.060, 0.245; 2.149,
0.229; 2.248, 0.211;
1.711, 0.263; 1.786, 0.263; 1.873, 0.252; 1.972, 0.240; 2.053, 0.229; 2.126, 0.219; 2.211,
0.206; 2.307, 0.188; 2.426, 0.167; 2.518, 0.150; 2.621, 0.131; 2.668, 0.123; 2.721, 0.113;
2.784, 0.103; 2.862, 0.0908; 2.933, 0.0794; 2.953, 0.0768;
2.967, 0.0865; 3.028, 0.0764; 3.080, 0.0683; 3.124, 0.0616; 3.161, 0.0561; 3.207, 0.0517;
2.997, 0.0822; 3.023, 0.0777; 3.053, 0.0735; 3.086, 0.0691; 3.121, 0.0647; 3.159, 0.0602;
3.186, 0.0572; 3.229, 0.0525; 3.278, 0.0479; 3.312, 0.0465; 3.346, 0.0414; 3.384, 0.0381;
3.428; 0.0348; 3.476, 0.0314;
3.553, 0.0243; 3.600, 0.0209; 3.631, 0.0183; 3.609, 0.0180; 3.678, 0.0138; 3.744, 0.0113;

$[BHCl]_{org} = 0.0150$ M
1.604, 0.356; 1.687, 0.337; 1.866, 0.303; 2.064, 0.259; 2.210, 0.232; 2.301, 0.200;
1.608, 0.335; 1.689, 0.323; 1.774, 0.307; 1.865, 0.292; 1.965, 0.278; 2.059, 0.261; 2.151,
0.245; 2.235, 0.229; 2.313, 0.214; 2.386, 0.201; 2.445, 0.188; 2.507, 0.177; 2.560, 0.167;
2.607, 0.158; 2.688, 0.142; 2.818, 0.118;
1.666, 0.344; 1.744, 0.324; 1.833, 0.309; 1.933, 0.295; 2.024, 0.276; 2.114, 0.258; 2.200,
0.241; 2.281, 0.225; 2.354, 0.211; 2.477, 0.185; 2.582, 0.164; 2.670, 0.147;
1.673, 0.335; 1.847, 0.300; 2.060, 0.271; 2.233, 0.235; 2.386, 0.205; 2.505, 0.180; 2.579,
0.159;
2.451, 0.185; 2.505, 0.176; 2.563, 0.166; 2.622, 0.156; 2.748, 0.135; 2.855, 0.115; 2.956,
0.101; 3.039, 0.0888;
3.001, 0.110; 3.135, 0.0873; 3.229, 0.0720; 3.302, 0.0611; 3.402, 0.0534; 3.332, 0.0665;
3.497, 0.0475; 3.655, 0.0333; 3.798, 0.231; 3.983, 0.157; 3.939, 0.0156; 3.977, 0.0126;
4.071, 0.00963; 4.114, 0.00832; 4.176, 0.00701;
3.557, 0.0328; 3.704, 0.0230; 3.878, 0.0190; 3.949, 0.0151; 4.056, 0.00992; 4.125, 0.00741;
4.166, 0.00589; 4.198, 0.00490; 4.240, 0.00366;

$[BHCl]_{org} = 0.220$ M
1.611, 0.355; 1.657, 0.346; 1.718, 0.344; 1.768, 0.334; 1.822, 0.325; 1.878, 0.316; 1.937,
0.307; 2.001, 0.298; 2.054, 0.288;
1.789, 0.333; 1.874, 0.320; 1.963, 0.305; 2.059, 0.291; 2.152, 0.275; 2.254, 0.260; 2.338,
0.244; 2.419, 0.230; 2.497, 0.216; 2.570, 0.204; 2.634, 0.192;
2.102, 0.289; 2.230, 0.267; 2.360, 0.246; 2.477, 0.226; 2.583, 0.207; 2.676, 0.190; 2.764,
0.176; 2.830, 0.162;
2.272, 0.260; 2.415, 0.233; 2.608, 0.202; 2.787, 0.173; 2.978, 0.139; 3.125, 0.115; 3.300,
0.0890; 3.500, 0.0620; 2.977, 0.145; 3.071, 0.128; 3.213, 0.102; 3.382, 0.0774; 3.532, 0.0566;
3.657, 0.0419; 3.775, 0.0307; 3.933, 0.0193; 3.989, 0.0161;
2.655, 0.202; 2.802, 0.176; 2.934, 0.155; 3.042, 0.138; 3.154, 0.124; 3.225, 0.112;
3.102, 0.130; 3.233, 0.111; 3.330, 0.0960; 3.431, 0.0848; 3.482, 0.0757; 3.264, 0.103; 3.347,
0.0879; 3.416, 0.0764; 3.497, 0.0678; 3.533, 0.0606; 3.570, 0.0548; 3.650, 0.0443; 3.710,
0.0371;
3.573, 0.0584; 3.644, 0.0492; 3.705, 0.0426; 3.752, 0.0375; 3.801, 0.0335; 3.823, 0.0302;
3.853, 0.0275; 3.922, 0.0226; 3.970, 0.0191;

$[BHCl]_{org} = 0.300$ M
1.634, 0.342; 1.695, 0.334; 1.764, 0.328; 1.828, 0.318; 1.897, 0.308; 1.968, 0.298, 2.060,
0.290;
1.776, 0.334; 1.825, 0.326; 1.876, 0.318; 1.935, 0.312; 1.996, 0.305; 2.050, 0.296; 2.107,
0.287; 2.170, 0.279; 2.214, 0.268;
1.961, 0.313; 2.024, 0.301; 2.096, 0.292; 2.166, 0.281; 2.238, 0.270; 2.306, 0.259; 2.374,
0.249; 2.443, 0.239; 2.507, 0.229; 2.575, 0.220; 2.632, 0.211; 2.691, 0.203; 2.742, 0.195;
2.448, 0.246; 2.629, 0.216; 2.668, 0.210; 2.725, 0.201; 2.776, 0.192; 2.823, 0.184; 2.886,
0.174; 2.942, 0.165; 2.996, 0.156; 3.058, 0.148; 3.100, 0.141; 3.146, 0.135;

2.933, 0.173; 2.977, 0.166; 3.017, 0.160; 3.064, 0.152; 3.107, 0.145; 3.151, 0.138; 3.193, 0.131; 3.244, 0.123; 3.291, 0.115; 3.333, 0.109; 3.374, 0.103; 3.406, 0.0974; 3.463, 0.0881; 3.517, 0.0806;
3.436, 0.0982; 3.456, 0.0953; 3.517, 0.0872; 3.570, 0.0803; 3.617, 0.0745; 3.727, 0.0652; 3.786, 0.0579; 3.840, 0.0519;
3.846, 0.0480; 3.955, 0.0376; 4.064, 0.0292; 4.209, 0.0207; 4.338, 0.0149; 4.473, 0.0101; 4.539, 0.00797; 4.326, 0.0169; 4.380, 0.0135.

The values of $[Fe(III)]_{aq}$ have been calculated from the measured equilibrium emf according to eqn. (2) using the following assumptions:

1. The ratio $\sum_0^n [FeCl_n^{3-n}]/[Fe^{3+}]$ and the analogous one for Fe(II) are constant. Each ion extracted into the organic phase carries along three chloride anions, which results in the decrease of the total concentration of chloride ions in the aqueous phase. This effect can certainly be neglected in the range log $[Fe(III)]_{aq} < -3$. To diminish the decrease of the concentration of Cl^- ions the ratio V_{org}/V_{aq} was kept as low as possible. In some of the titrations the ionic medium was adjusted by addition of the 1.9 M LiCl + 0.1 M HCl solution after each step in the titration. The data obtained in this way agree well within experimental error with data obtained by titration without addition of LiCl (see Fig. 3).

2. As was discussed earlier, there is no reliable information regarding the extraction of Fe(II) by BHCl. For that reason two cases were considered: (1) that the changes in the aqueous concentration of Fe(II) are negligible, (2) that the data in Fig. 1 represent the distribution of Fe(II) only. The aqueous concentration of Fe(III) for the second case was calculated from

$$\log [Fe(III)]_{aq, corr} = \log [Fe(III)]_{aq} - \log (k[BHCl]^2 V_{org}/V_{aq} + 1) \qquad (5)$$

where k is the apparent equilibrium constant of reaction (3) ($k = 0.19 \pm 0.05$), V_{org} and V_{aq} the volumes of the organic and the aqueous phases and [BHCl] is the concentration of free BHCl, calculated for the "best" set of complexes by means of the computer program Haltafall.[12]

The highest values of log $[Fe(III)]_{aq, corr}$ — log $[Fe(III)]_{aq} = -0.002$, which corresponds approximately to the accuracy of the potentiometer, but
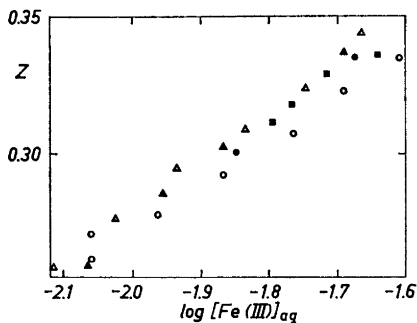

Fig. 3. Enlarged part of Fig. 1 showing data for titrations where the 1.0 M (Fe(III), Fe(II), 0.1 M H$^+$, Li$^+$)Cl$^-$ ionic medium was adjusted after each point (full symbols) and for titrations without adjustments (open symbols). [BHCl]$_{org}$ = 0.150 M.

in most cases the difference is well below this value. The highest deviation $Z_{corr} - Z$ found was one unit in the last figure of the Z-values given in Table 1.

TREATMENT OF DATA

The equilibrium aqueous phases contained 0.1 M HCl. Therefore no hydrolyzed iron species need to be considered and TLA is practically completely converted to the ammonium salt.[1] The general equilibrium reaction can be written in the following way:

$$p\text{FeCl}_n^{3-n}(\text{aq}) + p(3 - n)\,\text{Cl}^-(\text{aq}) + q\text{BHCl}(\text{org}) \rightleftharpoons (\text{FeCl}_3)_p(\text{BHCl})_q(\text{org}) \quad (6)$$

$$k_{p,q} = [(\text{FeCl}_3)_p(\text{BHCl})_q] C_{\text{Fe(III), aq}}^{-p} [\text{BHCl}]^{-q} \quad (7)$$

Although no information about the distribution of the chloride ions was obtained, the way they were included into eqn. (6) seems reasonable for there is no evidence for any free ionic species or mixed ligand (like chloro-hydroxo) complexes in the organic phase. In the following the complexes are referred to as (p, q).

Considering the evidence brought by distribution studies with tracer Fe(III) and the study of the aggregation of BHCl, three mechanisms of extraction of Fe(III) can be proposed:

I. The complexes (p, q) have rather small p and q. The aggregation of BHCl is neglected, *i.e.* B is assumed to be in the form of the (0,1) complex only.

II. The complexes (p, q) are of moderate size again, but the aggregation of BHCl found by Högfeldt and Tavares [1] is taken into account.

III. Both the BHCl and iron complexes are aggregated.

For the first mechanism the averages $\bar{p}$ and $\bar{q}$, defined by eqn. (8) were calculated.

$$\bar{p} = \Sigma p C_{pq} / \Sigma C_{pq}, \quad \bar{q} = \Sigma q C_{pq} / \Sigma C_{pq} \quad (8)$$

By C_{pq} is denoted the concentration of the complex (p, q). The calculations were made for the data given in Table 1 (log [Fe(III)]$_{aq}$, Z) according to Sillén [13] and using the computer program MESAK.[14] From Fig. 4, where $\bar{p}$ is plotted against $\bar{q}$, the predominating complexes seem to be those with $p = 1$ and $q = 1$, 2, 3. The treatment mentioned is not applicable for complexes $(0,q)$ and therefore it was not possible to make analogous calculations for mechanisms II and III.

The final analysis of the data was made with the computer program LETAGROPVRID,[15] searching for the set of values $(p, q, k_{p,q})$ that would minimize the error square sum U, defined by

$$U = \sum_1^{n_p} (Z_{calc} - Z_{exp})^2 \quad (n_p = \text{number of experimental points}) \quad (9)$$

For mechanism I and II the following complexes were tried: 1,1; 1,2; 1,3; 1,4; 1,5; 2,1; 2,2; 2,3; 2,4; 2,5; 3,1; 3,2; 3,3; 3,4; 3,5; 3,6; 4,4; 4,6; 4,8; 4,12. The composition of the aggregates of BHCl (0,3 and 0,48 which represents the
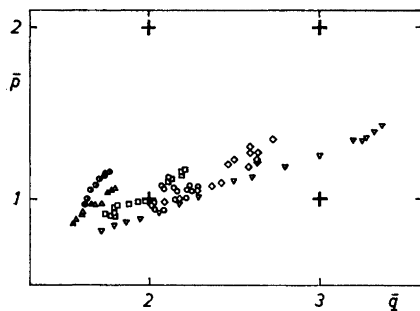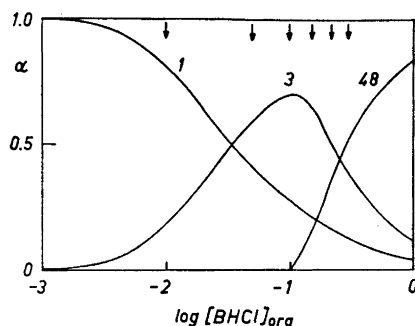
large aggregates) and their equilibrium constants were taken from the work of Högfeldt and Tavares[1] and were not varied in the course of calculation.

According to the idea underlying mechanism III, the size of the aggregates of the iron complexes is related to the size of BHCl aggregates. In Fig. 5 the relative proportions of various BHCl aggregates are given, as calculated from the data given by Högfeldt and Tavares[1] for 0.1 M HCl in the aqueous phase. The arrows indicate the concentrations of BHCl used in the present study. In the region where both the (0,3) and (0,48) aggregates are present, the number of conceivable (*p,q*)-combinations is too great for simultaneous treatment and besides the composition (0,48) is merely a formal description for a possible number of higher aggregates. The calculations for mechanism III were performed therefore only for the lower concentration of BHCl (0.01 M, 0.05 M, and 0.10 M) where only the (0,3) aggregate is to be considered.

The summary of the calculations with "the best" sets of complexes is given in Table. 2.

DISCUSSION

According to the results of computation given in Table 2 the values of $\sigma(Z)$ for the best sets of both mechanisms I and III are of comparable magnitude. However, III may be carried to a closer fit by considering a larger number of species. Since BHCl is aggregated to a high extent,[1,2] which was neglected for the first mechanism proposed, mechanism I is to be interpreted as a mere simplification of the real mechanism III. Both monomers and aggregates of BHCl seem to form iron complexes equally well and the metal complexes formed are aggregated also. The type of bond in metal-alkylammonium salt complexes, the dipole-dipole interactions between the simplest species in the organic phase, the ion pairs (BH^+Cl^-) and ($BH^+FeCl_4^-$), could give rise to clusters of various size, similar to those formed with pure BHCl.

Table 2. The best sets of complexes and their equilibrium constants and standard deviations in Z for different mechanisms describing the extraction of Fe(III) from 1.0 M Cl⁻, 0.1 M H⁺ aqueous solutions by trilaurylammonium chloride dissolved in o-xylene.

Mechanism	Set of complexes (p,q)	$\log(k_{p,q} \pm 3\sigma(k_{p,q}))$	$\sigma(Z)$
I	1,1; 1,2; 1,3	1.03 ± 0.03, 2.75 ± 0.03, 3.68 ± 0.05	0.0087
	1,1; 1,2; 1,4	0.92 ± 0.05, 2.90 ± 0.02, 4.39 ± 0.09	0.011
	1,2; 1,3	3.01 ± 0.03, 3.27 ± 0.22	0.020
	1,1; 1,2	0.79 ± 0.09, 2.93 ± 0.03	0.017
II	0,3; 0,48; 1,4; 2,5; 3,5;	3.03 nv[a], 69.27 nv, 7.59 ± 0.06, 11.02 ± 0.16, 12.46 ± 0.18	0.024
	0,3; 0,48; 1,2; (1,1 rej[b])	3.03 nv, 69.27 nv, 3.90 ± 0.05	0.063
III[c]	0,3; 1,2; 3,1; 3,10	3.03 nv, 3.13 ± 0.15, 5.41 ± 0.09, 3.81 ± 0.14, 21.38 ± 0.25	0.0095
	0,3; 1,1; 3,3; 3,9	3.03 nv, 0.89 ± 0.08, 5.50 ± 0.04, 7.70 ± 0.18, 19.46 ± 0.22	0.0094
	0,3; 1,2; 3,4	3.03 nv, 3.24 ± 0.10, 5.47 ± 0.06, 9.56 ± 0.25	0.012

[a] nv — aggregates of BHCl in o-xylene found by Högfeldt and Tavares.[1] Their equilibrium constants were not varied in the course of computer calculations.

[b] rej — complex was rejected in the course of computer calculations.

[c] for the computer calculations were used only data for $[BHCl]_{org} = 0.01$ M, 0.05 M, and 0.10 M.

The conclusions about the size of complexes, made from the equilibrium analytical data, depend primarily on the accuracy of the description of the aggregates of BHCl. It would be desirable to obtain some additional data by other methods about the size of both BHCl and metal ammonium salt species, especially for the region of high concentration of BHCl where the higher aggregates of BHCl predominate. Such determinations are scarce for the present, nevertheless they do not contradict our general conclusions about the mutual relationship between the size of alkylammonium salt and metal complex aggregates. Allen [16] has found by light scattering and isopiestic measurements that both the trioctylammonium sulfate and its uranyl sulfate complex are monomeric. Catrall and West claim to have determined by osmometry the degree of association of the Fe(III) complex with the secondary di(3,5,5-trimethylhexyl)ammonium sulfate to be 3.6 in benzene.[17] In the solution of the ammonium sulfate only they have found by light scattering aggregates containing up to 48 molecular units.[18]

The conclusions obtained from the experiments with tracer concentrations of Fe(III), e.g. by White et al.[4] or Good and Bryan [19] give the gross metal to amine ratio in various complexes, thus providing an idea about the type of metal complexes, but neglecting their degree of aggregation.

Mechanism II, which implies that monomeric BHCl is the only complex forming species, seems to be ruled out.

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