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Solvent Extraction of Iron(III) in Concentrated Nitric Acid with Several β-Diketones

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Synopsis. The solvent extraction of iron(III) in nitric acid (1 to 13.2 mol dm^{-3}) with seven β-diketones into carbon tetrachloride was studied. The extraction curve has a pronounced minimum at from 6 to 7 mol dm^{-3} acid, and the extracted iron(III) species were assumed to be represented by $FeA_a(NO_3)_{3-a}(HA)_n$ (where a and n are from 0 to 3).

The solvent extraction of metal ions with weakly acid chelating extractants(HA) is dependent on the concentration of its dissociated form(A^-), and the distribution ratio increases when the hydrogen-ion concentration is decreased. The extraction of iron(III) with β-diketones such as 2-thenoyltrifluoroacetone (TTA) also shows the above tendency.[1] However, the extractions of metal ions in concentrated acid solutions with weakly acid chelating extractants have also been reported by some authors.[2] For example, titanium(IV) in concentrated hydrochloric acid was extracted with β-diketones.[3] The extractions of zirconium(IV) and hafnium(IV) from concentrated nitric, hydrochloric, and perchloric acid with TTA and *N*-benzoyl-*N*-phenylhydroxylamine are other examples.[4–6] It was also reported that iron(III) was extractable even from concentrated nitric acid with TTA in xylene and that the distribution ratio increased upon an increase in the acid concentration.[7] This extraction was further studied;[8] it was reported that iron(III) was extractable with TTA in xylene both from 10 mol dm^{-3} nitric acid and 10 mol dm^{-3} ammonium nitrate, and that the rate of extraction was higher from the former than the latter. An increase in the rate of the extraction of iron(III) with TTA by the addition of nitrate was also reported and the extraction of the $FeA_2{}^+NO_3{}^-$ species was assumed in addition to the FeA_3, although no further details were given.[9]

Experimental

The experiments were carried out at 25±0.3 °C. All the reagents were of an analytical grade. An iron(III) solution prepared by dissolving metallic iron in nitric acid (in some cases, in an acid sodium nitrate solution) and a carbon tetrachloride solution of a β-diketone were placed in a stoppered glass tube, agitated, and centrifuged. Some extractions with TTA was also made by using chloroform as the diluent. In some cases, the iron(III) extracted into the organic phase was agitated with a fresh nitric acid solution and centrifuged. The iron(III) in the organic phase was stripped by a 6 mol dm^{-3} portion of hydrochloric acid. This back-extracted iron(III) and the iron(III) in the equilibrated aqueous phase was determined by atomic absorption, and the distribution ratio was calculated as;

$$D=[\mathrm{Fe(III)}]_{\mathrm{org}}/[\mathrm{Fe(III)}]. \qquad (1)$$

Results and Discussion

The β-diketones used were as follows: acetylacetone (AA), benzoylacetone(BZA), dibenzoylmethane(DBM), trifluoroacetylacetone (TFA), 2-thenoyltrifluoroacetone (TTA), benzoyltrifluoroacetone(BFA), and hexafluoroacetylacetone(HFA). When the acid concentration was high, the rate of extraction was high; agitation for 1 min was enough to achieve the equiribrium. However, when the acid concentration was lower than 6 mol dm^{-3}, it was low; the extraction of iron(III) in 1 mol dm^{-3} of nitric acid with 0.2 mol dm^{-3} of TTA in chloroform did not reach equilibrium for at least 3 h. In such cases, the distribution ratio at equiribrium was estimated from the extrapolation of the data of the forward extraction from the aqueous phase and of the backward extraction from the organic phase, which had extracted the iron(III) with that β-diketone.

Figure 1 gives the dependence of D on the nitric acid concentration. The extraction with AA was too poor to be determined, and that with HFA was not reproducible for unknown reasons, although its magnitude was between that with TFA and DBM. Judging from these facts, the order of extractability with these β-diketones is: TTA > BFA > TFA > (HFA) > DBM > BZA > AA. As may be seen from Fig. 1, each

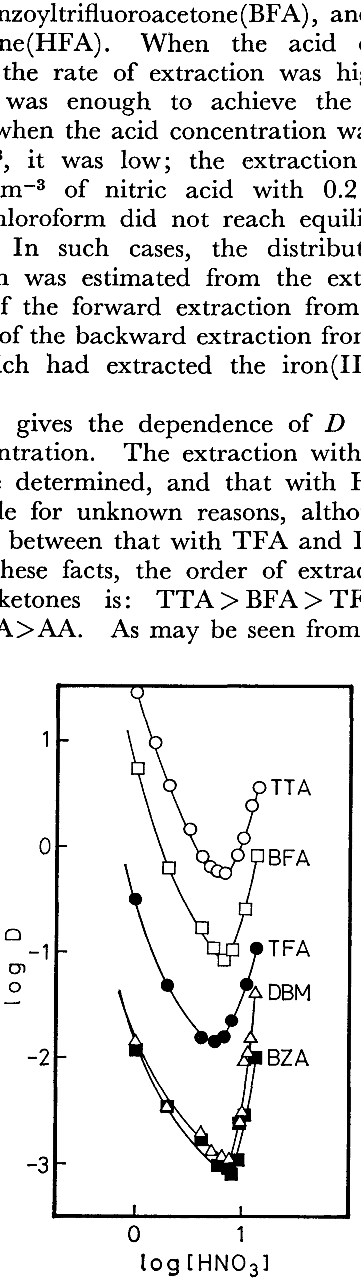

Fig. 1. Distribution ratio of Fe(III) as a function of nitric acid concentration.

Org. phase: CCl_4 initially containing 0.2 mol dm^{-3} of each β-diketone, aq. phase: nitric acid initially containing 5×10^{-4} to 1×10^{-3} mol dm^{-3} Fe(III).

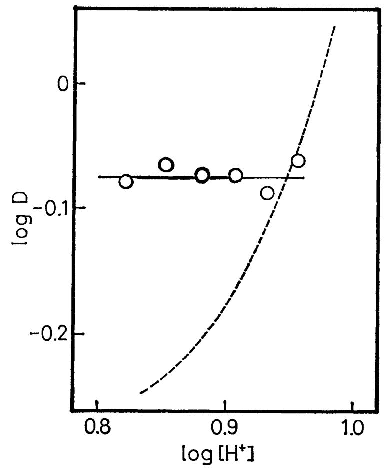

Fig. 2. Dependence of the distribution ratio on H^+ concentration when the aqueous phase was 9.1 mol dm^{-3} (H, Na)NO_3.
Org. phase: CCl_4 containing 0.2 mol dm^{-3} TTA. The broken line gives the extraction curve when the aqueous phase contains only nitric acid (*cf.* Fig. 1).

extraction curve has a pronounced minimum at about 6 to 7 mol dm^{-3} of the acid. The dependence of the extraction on the β-diketone was determined when the aqueous phase was 13.2 mol dm^{-3} of nitric acid. The slope of the log D *vs.* log $[HA]_{org}$ plot was +3 with TTA, BFA, TFA, and HFA, while it was +2 with DBM and BZA. Figure 2 shows that the extraction with TTA is independent of the hydrogen-ion concentration when the nitrate concentration was 9.1 mol dm^{-3}. The extraction with TTA was also studied by using chloroform as the diluent. It was found that the shape of the curve was rather similar, but the distribution ratio was three to five times higher when the diluent was carbon tetrachloride.

The color of the organic phase which extracted iron(III) from concentrated nitric acid with these β-diketones was similar to that which extracted iron(III) from 1 mol dm^{-3} of nitric acid, except in the case of BZA. The aqueous phase at equiribrium was nearly colorless when the acid concentration was 1 mol dm^{-3} but it was green (TTA and DBM), violet (AA and BZA), pink(BFA and TFA), or colorless (HFA) when the acid was above 6 mol dm^{-3}; the higher the acid concentration, the deeper the color.

Since the ionic concentration in the aqueous phase in Fig. 1 changes with the acid concentration, a quantitative discussion covering all the acid concentration region is difficult. However, since the distribution ratio in Fig. 2 is independent of the hydrogen-ion concentration, the β-diketone in its undissociated form, HA, is assumed to combine with iron(III) nitrate complexes when the nitrate concentration is high. The finding that two molecules of BZA or DBM were enough to extract iron(III) from concentrated nitric acid also seems to support this assumption.

It has been pointed out that the rate of the extraction of iron(III) from acid solutions with the β-diketones as their tris-complexes was low.[10,11] The rate of extraction at low acid concentrations in the present study agrees with this previous finding. The rapid extraction in the concentrated acid region also suggests that type of extraction in this region is different. The observation that an increase in the nitric acid concentration increased the distribution ratio in Fig. 1 may be explained by an increase in the concentration of the iron(III) nitrate complexes (a "salting-out" effect may also contribute). The better extraction when the diluent was carbon tetrachloride than when it was chloroform is similar to the general tendency when solvating-type extractants such as tributyl phosphate are used;[2] this also supports the extraction of the $Fe(NO_3)_3$ complex with two or three molecules of undissociated form β-diketones. Thus, the species extracted from dilute acid solutions should be in the FeA_3 form, but the extracted species should be in the $Fe(NO_3)_3(HA)_n$ (where n is 2 or 3) form from concentrated acid solutions. The extracted species in the intermediate region should be, consequently, mixtures of these two species and the mixed complexes in the form of $FeA_a(NO_3)_{3-a}(HA)_n$ (where a is 1 or 2 and n is smaller than 3). However, an accurate estimation of the composition in the organic phase in this region seems to be difficult because the shape of the absorption curves of the organic phase is not very much affected by the acid concentration, and also because the determination of the molar ratio of Fe^{3+} and NO_3^- in the organic phase by chemical analysis is difficult due to the large amount of nitric acid co-extracted.

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