BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (9), 2629—2630 (1976)

Solvent Extraction Equilibria of Acids. IV. Tetrachloroferric Acid in a Hexane Containing Trioctylphosphine Oxide-Aqueous Chloride Solution System

Tatsuya SEKINE, Yoshiyuki ZENIYA, and Masaru NIITSU*
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
**Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02*

(Received October 7, 1975)

Synopsis. From the distribution ratio of iron(III) between hexane containing trioctylphosphine oxide (TOPO) and a 4 mol dm^{-3} aqueous (H, Na)Cl solution, the extraction constants for the two complexes, $K_{\mathrm{ex}_3}=[\mathrm{FeCl_3(TOPO)_2}]_{\mathrm{org}}$-$[\mathrm{Fe^{3+}}]^{-1}[\mathrm{Cl^-}]^{-3}[\mathrm{TOPO}]_{\mathrm{org}}{}^{-2}$ and $K_{\mathrm{ex}_4}=[\mathrm{HFeCl_4(TOPO)_2}]_{\mathrm{org}}$-$[\mathrm{Fe^{3+}}]^{-1}[\mathrm{H^+}]^{-1}[\mathrm{Cl^-}]^{-4}[\mathrm{TOPO}]_{\mathrm{org}}{}^{-2}$, were determined to be $10^{4.5}$ and $10^{4.3}$, respectively. The extractability of tetrachloroferric acid are discussed by comparing the K_{ex} value with that for perchloric acid.

Solvent extraction of iron(III) from hydrochloric acid with oxygen-containing solvents, such as diethyl ether, is one of the oldest applications of this method to metal ions[1,2] and, as reviewed by Diamond and Tuck[3] and Marcus and Kertes,[4] the extracted species is recognized to be tetrachloroferric acid, $\mathrm{HFeCl_4}$. In the present work, this extraction was reinvestigated using hexane containing a small amount of trioctylphosphine oxide (TOPO) as the organic phase and the equilibria in the system are discussed.

Experimental and Statistical

The experiments and the analysis of the data were performed in a similar manner to other studies in this series.[5-7] The stock iron(III) solution was prepared by dissolving ferric chloride in hydrochloric acid. All the procedures were performed in a room with the temperature thermostatically controlled at 25±0.3 °C. A portion of hexane containing TOPO and the same volume of an aqueous 4 mol dm^{-3} (H, Na)Cl solution containing 1×10^{-3} mol dm^{-3} iron(III) were placed in a stoppered glass tube, stirred vigorously for 15 min and centrifuged. The iron(III) content in the organic phase was determined from the optical absorption at 425 nm after it was colored by β-isopropyltropolone[8,9] and that in the aqueous phase was determined from the absorption at 480 nm after it was colored by thiocyanate.[10]

All the species in the organic phase are denoted by the subscript "org" and those in the aqueous phase by the lack of any subscript. The stability constants for iron(III) complexes in the aqueous phase are:

$$\beta_n = [\mathrm{FeCl}_n{}^{3-n}][\mathrm{Fe^{3+}}]^{-1}[\mathrm{Cl^-}]^{-n} \tag{1}$$

As will be seen below, the extraction constants for the trichloride and tetrachloride complexes of iron(III) can be written as:

$$K_{\mathrm{ex}_3} = [\mathrm{FeCl_3(TOPO)_2}]_{\mathrm{org}}[\mathrm{Fe^{3+}}]^{-1}[\mathrm{Cl^-}]^{-3}[\mathrm{TOPO}]^{-2}_{\mathrm{org}} \tag{2}$$

and

$$K_{\mathrm{ex}_4} = [\mathrm{HFeCl_4(TOPO)_2}]_{\mathrm{org}}[\mathrm{Fe^{3+}}]^{-1}[\mathrm{H^+}]^{-1} \times[\mathrm{Cl^-}]^{-4}[\mathrm{TOPO}]^{-2}_{\mathrm{org}} \tag{3}$$

The distribution ratio of iron(III) under the present conditions can be written as:

$$\begin{aligned} D &= [\mathrm{Fe(III)}]_{\mathrm{org,total}}[\mathrm{Fe(III)}]^{-1}_{\mathrm{total}} \\ &= ([\mathrm{FeCl_3(TOPO)_2}]_{\mathrm{org}}+[\mathrm{HFeCl_4(TOPO)_2}]_{\mathrm{org}}) \\ &\quad \times([\mathrm{Fe^{3+}}]+[\mathrm{FeCl^{2+}}]+[\mathrm{FeCl_2{}^+}])^{-1} \end{aligned} \tag{4}$$

By substituting Eqs. 1 through 3 into 4, we can write:

$$\begin{aligned} D &= \{[\mathrm{TOPO}]^2_{\mathrm{org}}(K_{\mathrm{ex}_3}[\mathrm{Cl^-}]^3+K_{\mathrm{ex}_4}[\mathrm{H^+}][\mathrm{Cl^-}]^4)\} \\ &\quad \times(1+\beta_1[\mathrm{Cl^-}]+\beta_2[\mathrm{Cl^-}]^2)^{-1} \end{aligned} \tag{5}$$

and thus,

$$\begin{aligned} &\log\{D(1+\beta_1[\mathrm{Cl^-}]+\beta_2[\mathrm{Cl^-}]^2)[\mathrm{Cl^-}]^{-3}[\mathrm{TOPO}]^{-2}_{\mathrm{org}}\} \\ &\quad = \log(K_{\mathrm{ex}_3}+K_{\mathrm{ex}_4}[\mathrm{H^+}][\mathrm{Cl^-}]) \end{aligned} \tag{6}$$

The values of these extraction constants can be obtained by a curve-fitting method using the following standard curve:[12]

$$Y = \log(1+v), \quad X = \log v \tag{7}$$

Results and Discussion

The slope of the log D *vs.* log $[\mathrm{TOPO}]_{\mathrm{org}}$ plot was +2 for hydrogen-ion concentrations of the 4 mol dm^{-3} chloride solution of either 1×10^{-2} or 1 mol dm^{-3}. The extraction of iron(III) in 4 mol dm^{-3} chloride solutions increased with an increase in the hydrogen-ion concentration. Figure 1 shows the log D *vs.* log $[\mathrm{H^+}]$ plot.

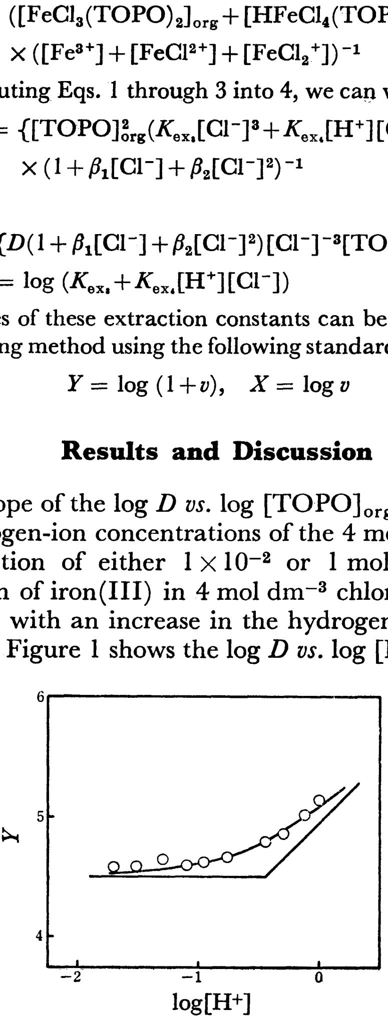

Fig. 1. Increase in the distribution ratio of Fe(III) as a function of the hydrogen-ion concentration. Org. phase: hexane initially containing 3×10^{-3} mol dm^{-3} TOPO. Aq. phase: 4 mol dm^{-3} (H, Na)Cl. The ordinate is $Y=\log\{D(1+\beta_1[\mathrm{Cl^-}]+\beta_2[\mathrm{Cl^-}]^2)[\mathrm{Cl^-}]^{-3}\times[\mathrm{TOPO}]_{\mathrm{org}}{}^{-2}\}$. The solid curve is obtained by introducing the extraction constants K_{ex_3} and K_{ex_4} into Eq. 6.

From the dependence of D on the hydrogen-ion and TOPO concentrations described above, the extracted species are assumed to be mainly $\mathrm{FeCl_3(TOPO)_2}$ and $\mathrm{HFeCl_4(TOPO)_2}$ in the lowest and highest hydrogenion concentration regions, respectively. Using the stability constants previously obtained in 4 mol dm^{-3} aqueous Na(Cl, $\mathrm{ClO_4}$) medium[11]· ($\beta=10^{0.88}$ and $\beta_2=10^{0.80}$, those of the higher complexes being negligibly small) and by correcting for the free TOPO concentration due to the extraction of hydrochloric acid, the data were analyzed by the curve-fitting method. The constants in Eqs. 2 and 3 were determined to be $K_{ex_3}=10^{4.5}$ and $K_{ex_4}=10^{4.3}$, respectively. The solid curve in Fig. 1 was calculated by introducing these constants into Eq. 6.

The extraction of iron(III) chloride with TOPO has been reported previously,[11,13–15] but the equilibria involved have not been discussed in detail.

The dissociation of $HFeCl_4$, a very strong acid which is comparable to perchloric acid,[3,4] should be negligible in hexane containing a small amount of TOPO as in the case of perchloric acid already discussed,[5] and therefore, Eqs. 2—6 can be applied for the present data. On the other hand, the dissociation of this acid should be taken into account in various polar organic solvents saturated in water. This may be one of the reasons why the extraction constant in Eq. 3 has never been reported in previous reports on iron(III) chloride extraction.

The solvation number of $HFeCl_4$ has also been found to be two with respect to tributylphosphate (TBP).[16] The IR absorption of TBP in benzene due to the stretching vibration of the phosphoryl group has been systematically studied.[17] It was found[17] that the shift of the TBP absorption band to lower frequencies upon extracting iron(III) from 6 mol dm^{-3} hydrochloric acid was similar to that which occurred with the TBP solvating nitrates of lanthanoides. Thus it should be reasonable to assume that since the central metal ion should be coordinated to TBP in the extracted iron(III) complex of that report, the TOPO molecules in the present study should be bound to $HFeCl_4$ through a coordination bond, but not to the proton through a hydrogen-bond.

In previous work,[11] neither the $FeCl_3$ nor the $FeCl_4^-$ complex was detected in 4 mol dm^{-3} aqueous chloride solutions to within the limit of experimental error and thus the determination of the following extraction constant was not possible from the present data:

$$K_{ex}(\text{acid}) = [\text{HX(TOPO)}_2]_{org}[\text{H}^+]^{-1}[\text{X}^-]^{-1}[\text{TOPO}]_{org}^{-2} \quad (8)$$

However, on assuming that β_4 is smaller than 10^{-1}, the lower limit of the constant in Eq. 8 for the tetrachloroferric acid (X^- is $FeCl_4^-$) was estimated to be $K_{ex}(HFeCl_4)>10^{5.3}$, which is more than ten times the value for perchloric acid (X^- is ClO_4^-) in the 4 mol dm^{-3} ionic medium with TOPO in hexane[9] ($K_{ex}(HClO_4)=10^{4.16}$). Since perchloric acid is known to be one of the most extractable inorganic acids using solvating type extractants,[3–5] one possible explanation for the high extractability of this complex acid may be given as follows: the TOPO molecules are coordinated to the central iron(III) in the complex. However, further information is necessary before a final conclusion can be drawn.

The authors are very grateful to Dr. Akira Yamasaki of the Electrocommunications University, Tokyo, for valuable discussions concerning this work.

References

1) M. Hanroit, *Bull. Soc. Chim. Fr.*, **7**, 171 (1892).
2) J. W. Rothe, *Chem. News.*, **66**, 182 (1892).
3) R. M. Diamond and D. G. Tuck, *Prog. Inorg. Chem.*, **2**, 109 (1960).
4) Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience, New York (1969), p. 575.
5) T. Sekine and M. Niitsu, *J. Inorg. Nucl. Chem.*, **37**, 1054 (1975).
6) M. Niitsu and T. Sekine, *J. Inorg. Nucl. Chem.*, **38**, 1053 (1976).
7) M. Niitsu and T. Sekine, *J. Inorg. Nucl. Chem.*, **38**, 1057 (1976).
8) D. Dyrssen, *Trans. Royal Inst. Technolog. Stockholm, No.* **188** (1962).
9) T. Sekine, H. Honda, and Y. Zeniya, *J. Inorg. Nucl. Chem.*, **38**, 1347 (1975).
10) E. B. Sandell, "Colorimetric Determination of Traces of Metals" Interscience, New York (1959) p. 522.
11) T. Sekine and T. Tetsuka, *Bull. Chem. Soc. Jpn.*, **45**, 1620 (1972).
12) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1727 (1964).
13) J. O. Hibbits, W. F. Davis, and M. R. Menke, *Talanta*, **4**, 61 (1960).
14) J. O. Hibbits, W. F. Davis, and M. R. Menke, *Talanta*, **8**, 164 (1961).
15) T. Ishimori and E. Nakamura, "Data of Inorganic Solvent Extraction" Res. Rept. Jpn. At. Energy Res. Inst., JAERI-**1047** (1963).
16) T. Ishimori, K. Watanabe, and T. Fujino, *Nippon Genshiryoku Gakkai Shi*, **3**, 19 (1961).
17) N. Saito and A. Yamasaki, *Bull. Chem. Soc. Jpn.*, **36**, 1055 (1963).