Synergistic Extraction of Manganese(II) and Iron(II) with Monothiothenoyltrifluoroacetone and 1,10-Phenanthroline

Hiroshi KAWAMOTO, Tsunemi AIBA and Hideo AKAIWA

Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376

The synergistic extraction of manganese(II) and iron(II) with monothiothenoyltrifluoroacetone (STTA=HR) and 1,10-phenanthroline (phen=S) was examined. The main species extracted into chloroform phase were found to be MnR_2S and FeR_2S_2 . This extraction system was applied to the quantitative separation of iron(II) from manganese(II). By the aid of phen, the extraction curves for both cations could be shifted to a lower pH region without losing the specificity of STTA toward iron(II).

Keywords Synergistic extraction, monothiothenoyltrifluoroacetone, 1,10-phenanthroline, manganese(II), iron(II)

Chaston *et al.* were the first to prepare monothiothenoyltrifluoroacetone (STTA) as well as its nickel(II) chelate. They showed that STTA acts as a ligand.¹ Thereafter, various metal-STTA complexes were prepared^{2,3}, and STTA was then introduced into the field of solvent extraction.⁴ This reagent was applied to the spectrophotometric determination of mercury(II)⁵, and other elements.⁶ Although a synergistic extraction system of metal-STTA was studied⁷ and applied to the spectrophotometric determination of iron(II)^{8,9}, only a few works¹⁰ aiming the separation of metal ions have been reported.

In the present work, the synergistic effect of 1,10-phenanthroline (phen) on the extraction of manganese(II) and iron(II) with STTA was studied. The result was applied to the separation of iron(II) from manganese(II).

Experimental

Apparatus

A Hitachi Model 170-30 atomic absorption spectrometer equipped with manganese and iron hollow cathode lamps (Hamamatsu Photonics) was used. A Horiba Model F-80 pH analyzer and a Iwaki KM type shaker were also used.

Reagents

STTA and phen were obtained from Wako Pure Chemicals, and were used without further purification. Chloroform and all the other chemicals used were of guaranteed grade. Deionized water was used throughout.

Extraction procedure

Twenty cubic centimeters of an aqueous solution containing 2.00×10^{-5} mol dm^{-3} manganese(II) or iron(II), 1.5% hydroxylamine sulfate and 0.1 mol dm^{-3} sodium sulfate, whose pH was preliminarily adjusted by adding sulfuric acid or sodium hydroxide, was placed in a separatory funnel. An equal volume of chloroform solution containing STTA and phen was added; the mixture was then shaken vigorously for 10 min. After the phases were allowed to separate, manganese(II) or iron(II) remaining in the aqueous phase was determined with the atomic absorption spectrometer, and the pH was also measured. All experiments were carried out at room temperature (*ca.* 293 K). The distribution ratio of a metal(II) was defined as follows:

$$D = \frac{\text{The concentration of a metal in the } CHCl_3 \text{ phase}}{\text{The concentration of a metal in the } H_2O \text{ phase}} \quad (1)$$

Theoretical

By assuming that the main species extracted with STTA (HR) and phen (S) is MR_2S_n ($n=0,1,2$), the extraction reaction can be expressed by

where M^{2+} represents manganese(II) and iron(II), and the subscript *org* denotes the organic phase. The extraction constant is defined by Eqn (3). Strictly speaking, the species remaining in the aqueous phase should be expressed as $MR_iS_j^{2-i}$ ($i,j=0-3$), for which the formation reaction and the equilibrium constant are written by Eqns (4) and (5), respectively.

$$K_{\text{ex},n} = \frac{[\text{MR}_2\text{S}_n]_{\text{org}}[\text{H}^+]^2}{[\text{M}^{2+}][\text{HR}]_{\text{org}}^2[\text{S}]_{\text{org}}^n} \quad (3)$$

$$K_{i,j} = \frac{[\text{MR}_i\text{S}_j^{-i}][\text{H}^+]^i}{[\text{M}^{2+}][\text{HR}]_{\text{org}}^i[\text{S}]_{\text{org}}^j} \quad (5)$$

Then, the distribution ratio given by Eqn (1) can be written as

$$D = \frac{\sum_n [\text{MR}_2\text{S}_n]_{\text{org}}}{\sum_i \sum_j [\text{MR}_i\text{S}_j^{-i}]_{\text{org}}} \quad (6)$$

From Eqns (3), (5) and (6), we obtain

$$D = \frac{[\text{HR}]_{\text{org}}^2 \sum_n K_{\text{ex},n} [\text{S}]_{\text{org}}^n}{[\text{H}^+]^2 \sum_i \sum_j K_{i,j} [\text{HR}]_{\text{org}}^i [\text{S}]_{\text{org}}^j [\text{H}^+]^{-i}} \quad (7)$$

By neglecting the concentration of phen combined with a metal(II), the total phen concentration added to the extraction system is given by

$$\begin{aligned} [\text{S}]_{\text{tot}} &= [\text{S}]_{\text{org}} + [\text{S}] + [\text{HS}^+] \\ &= [\text{S}]_{\text{org}} \left(1 + \frac{1}{K_{\text{DS}}} + \frac{[\text{H}^+]}{K_{\text{DS}}K_{\text{HS}}} \right) \quad (8) \end{aligned}$$

where $K_{\text{DS}} = [\text{S}]_{\text{org}}[\text{S}]^{-1}$ and $K_{\text{HS}} = [\text{H}^+][\text{S}][\text{HS}^+]^{-1}$. Introducing the values $\log K_{\text{DS}} = 3.05$ and $\text{p}K_{\text{HS}} = 5.05^{11}$, Eqn (8) can be expressed as

$$[\text{S}]_{\text{tot}} = [\text{S}]_{\text{org}}(1.00 + 100[\text{H}^+]) \quad (9)$$

The total concentration of STTA can be written by Eqn (10), if the concentration of STTA combined with a metal(II) can be neglected compared with that of free STTA:

$$\begin{aligned} [\text{HR}]_{\text{tot}} &= [\text{HR}]_{\text{org}} + [\text{HR}] + [\text{R}^-] \\ &= [\text{HR}]_{\text{org}} \left(1 + \frac{1}{K_{\text{DR}}} + \frac{K_{\text{HR}}}{K_{\text{DR}}[\text{H}^+]} \right) \quad (10) \end{aligned}$$

where $K_{\text{DR}} = [\text{HR}]_{\text{org}}[\text{HR}]^{-1}$ and $K_{\text{HR}} = [\text{H}^+][\text{R}^-][\text{HR}]^{-1}$. By using $\log K_{\text{DR}} = 4.19$, which was obtained by Uhlemann and Mueller's method, and $\text{p}K_{\text{HR}} = 4.10^{12}$, Eqn (10) can be rewritten as

$$[\text{HR}]_{\text{tot}} = [\text{HR}]_{\text{org}} \left(1.00 + \frac{5.12 \times 10^{-9}}{[\text{H}^+]} \right) \quad (11)$$

Equations (9) and (11) enable us to calculate $[\text{S}]_{\text{org}}$ and $[\text{HR}]_{\text{org}}$, respectively.

Results and Discussion

The extraction of manganese(II)

If the presence of phen causes the formation of MnR_2S and if the main species remaining in the aqueous phase is Mn^{2+} , Eqn (7) can be written as

$$\log D = \log(K_{\text{ex},0} + K_{\text{ex},1}[\text{S}]_{\text{org}}) + 2 \log[\text{HR}]_{\text{org}} + 2\text{pH} \quad (13)$$

In the case that the above assumption is valid, a plot of $\log D$ against pH keeping $[\text{S}]_{\text{org}}$ and $[\text{HR}]_{\text{org}}$ constant will give a straight line with a slope of 2. As seen in Fig. 1, plots at a pH higher than 6 fall on a straight line

Fig. 1 Plots of $\log D(\text{Mn})$ against pH. STTA, 1.00×10^{-3} M; phen, A, 2.00×10^{-3} M; B, 2.00×10^{-4} M.

Fig. 2 Logarithmic plot of $D(\text{Mn})$ against STTA concentration. Phen, 2.00×10^{-3} M; pH 5.45.

having a slope of 2, although positive deviations due to unknown reasons are seen at the low pH region. Figure 2 shows a straight line whose slope is 2, indicating that Eqn (13) is valid. However, the reason for the positive deviation in the region of $\log[\text{HR}]_{\text{org}} < -3.5$ is still unknown. Equation (13) can be rewritten as

$$\log D = \log \frac{K_{\text{ex},0}[\text{HR}]_{\text{org}}^2}{[\text{H}^+]^2} + \log \left(1 + \frac{K_{\text{ex},1}[\text{S}]_{\text{org}}}{K_{\text{ex},0}} \right). \quad (14)$$

Equation (14) can be expressed by a normalized curve (15), by taking $X = K_{\text{ex},1}[\text{S}]_{\text{org}}K_{\text{ex},0}^{-1}$ and $Y = \log D - \log K_{\text{ex},0}[\text{HR}]_{\text{org}}^2[\text{H}^+]^{-2}$.

$$Y = \log(1+X). \quad (15)$$

As a result of curve-fitting, in which our data well fits Eqn (15) (Fig. 3), $\log K_{\text{ex},0} = -5.82$ and $\log K_{\text{ex},1} = -2.37$ were obtained.

The extraction of iron(II)

By assuming that the main complex in the organic phase is FeR_2S_2 , and that the species remaining in the aqueous phase are FeS_3^{2+} and FeRS_2^+ , Eqn (7) can be rewritten as

$$D = \frac{[\text{HR}]_{\text{org}}^2 K_{\text{ex},2}}{[\text{H}^+]^2 (K_{0,3}[\text{S}]_{\text{org}} + K_{1,2}[\text{HR}]_{\text{org}}[\text{H}^+]^{-1})}. \quad (16)$$

When the predominant species in the aqueous phase is FeRS_2^+ , Eqn (16) approximates to Eqn (17):

$$\log D = \log \frac{K_{\text{ex},2}}{K_{1,2}} + \log[\text{HR}]_{\text{org}} + \text{pH}. \quad (17)$$

Equation (17) suggests that a plot of $\log D$ against pH keeping $[\text{HR}]_{\text{org}}$ constant will give a straight line having a slope of unity, which agrees with the plot shown in Fig.

Fig. 3 Logarithmic plot of $D(\text{Mn})$ against phen concentration. —, the best fitted curve; STTA, 1.00×10^{-3} M; pH 5.46.

4. On the other hand, Eqn (16) can be rewritten as

$$\log D - 2 \log[\text{HR}]_{\text{org}} = \log \frac{K_{\text{ex},2}}{[\text{H}^+]^2} - \log K_{0,3}[\text{S}]_{\text{org}} - \log \left(1 + \frac{K_{1,2}[\text{HR}]_{\text{org}}}{K_{0,3}[\text{S}]_{\text{org}}[\text{H}^+]} \right). \quad (18)$$

By taking $Y = \log D - 2 \log[\text{HR}]_{\text{org}} - \log K_{\text{ex},2}[\text{H}^+]^{-2} + \log K_{0,3}[\text{S}]_{\text{org}}$ and $X = K_{1,2}[\text{HR}]_{\text{org}}K_{0,3}^{-1}[\text{S}]_{\text{org}}^{-1}[\text{H}^+]^{-1}$, Eqn (18) can be expressed by a normalized curve (19):

$$Y = -\log(1+X). \quad (19)$$

As seen in Fig. 5, the plots are located on the normalized curve, indicating that Eqn (18) is available. In the case that $K_{0,3}[\text{S}]_{\text{org}} \gg K_{1,2}[\text{HR}]_{\text{org}}[\text{H}^+]^{-1}$, Eqn (20) is obtained from Eqn (16):

Fig. 4 Plots of $\log D(\text{Fe})$ against pH. STTA, 1.00×10^{-3} M; phen, 2.00×10^{-3} M.

Fig. 5 Effect of STTA concentration on the extraction of iron(II). —, the best fitted curve; phen, 2.00×10^{-3} M; pH 5.10.

Fig. 6 Logarithmic plots of $D(\text{Fe})$ against phen concentration. Plot-STTA/M-pH: A- 1.00×10^{-3} -5.19; B- 2.00×10^{-3} -4.57; C- 1.00×10^{-4} -5.20.

$$\log D = \log \frac{K_{\text{ex},2}}{K_{0,3}} + 2 \log [\text{HR}]_{\text{org}} + 2 \text{pH} - \log [\text{S}]_{\text{org}} \quad (20)$$

In Fig. 6, a plot of $\log D$ against $\log [\text{S}]_{\text{org}}$ keeping $[\text{HR}]_{\text{org}}$ and pH constant is shown by a straight line having a slope of minus unity, as predicted by Eqn (20). All the above results indicate that Eqn (16) is applicable to the present system; $\log K_{\text{ex},2}K_{0,3}^{-1} = -5.75$, $\log K_{\text{ex},2}K_{1,2}^{-1} = -1.77$, and $\log K_{1,2}K_{0,3}^{-1} = -3.98$ were obtained. Since $\log [\text{FeS}_3^{2+}][\text{Fe}^{2+}]^{-1}[\text{S}]^{-3} = -21.3$,¹³ $\log K_{\text{ex},2} = 6.40$ and $\log K_{1,2} = 8.17$ could be estimated.

The separation of iron(II) from manganese(II)

The solid curves given in Fig. 7-B and 7-C for iron(II) were obtained by calculations using Eqn (20), which can be fitted well to the experimental results. However, the extraction curves estimated from Eqn (13) deviate from those obtained by experiments, and the degree of the deviation becomes larger at higher pH region, probably because of hydrolysis of manganese(II).

Although the separation of iron(II) from manganese(II) could be performed without the aid of phen (Fig. 7-A), the pH condition for quantitative separation was an alkaline medium, ca. pH 7.5, where the troublesome hydrolysis of metal ions might occur, as mentioned above. On the contrary, iron(II) could be separated quantitatively from manganese(II) at a slightly acidic region, ca. pH 5.0, by the addition of a small amount of phen (Fig. 7-B,C). The addition of the synergist shifts the extraction curves to lower pH region without losing the specificity of STTA toward iron(II).

Fig. 7 Extraction curves. Shaking time, 30 min; STTA, 1.00×10^{-3} M. Phen: A, none; B, 1.00×10^{-4} M; C, 2.00×10^{-4} M.

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