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Design for Separation of Indium(III) from Gallium(III) by Chelate Extraction on the Basis of HSAB Rule

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A method for design of separation scheme of In^{III} from Ga^{III} by chelate extraction was proposed on the basis of HSAB rule, which predicted that dithizone would be the most effective for the separation among various chelating agents. This prediction was confirmed through experiments.

Extraction constants for metal chelate (K_{ex}) were rationalized by HSAB rule, into which a dual parameter scale, strength (S_A) and soft (σ_A) factors of a metal ion (M^{z+}), was introduced:[1)]

$$\log K_{ex} + zpK_a = S_A S_B + \sigma_A \sigma_B \quad (1)$$

where pK_a, the subscripts A and B mean acid dissociation exponent of chelating agent, Lewis acid and base, respectively. And S_A and σ_A are defined by Eqs. 2 and 3:[1)]

$$S_A = -\frac{2\Delta S_h^o}{2.30R} \quad (2)$$

and

$$\sigma_A = \frac{\Delta H_f^o}{2.30RT} , \quad (3)$$

where ΔS_h^o, R, ΔH_f^o, and T denote the hydration entropy of a metal ion, the gas constant, the heat of formation of an aqueous metal ion and absolute temperature, respectively.

Then, the extraction of Ga^{III} and In^{III} (= M^{3+}) with a chelating agent (HR) is assumed to proceed according to Eq. 4:

$$M^{3+} + 3HR_{org} \rightleftharpoons MR_{3,org} + 3H^+, \quad (4)$$

where the subscript shows the organic phase. Assuming that $D^M = [MR_3]_{org}[M^{3+}]^{-1}$, Eq.

5 can be obtained:

$$\log D^{M} = \log K_{ex}^{M} + 3\log[HR]_{org} + 3pH. \qquad (5)$$

In this case, the separation factor (S.F.) is defined as,

$$\begin{aligned} S.F. &= \log D^{In} - \log D^{Ga} \\ &= \log K_{ex}^{In} - \log K_{ex}^{Ga} \end{aligned} \qquad (6)$$

Thus, the following equation is derived from Eqs. 1 and 6.

$$S.F. = (S_{In} - S_{Ga})S_{B} + (\sigma_{In} - \sigma_{Ga})\sigma_{B}. \qquad (7)$$

Equation 7 means that the degree of the separation could be predicted by the values of HSAB parameters. Now, the S_A and σ_A values of In^{III} and Ga^{III} can be calculated from reported data[2,3] and listed in Table 1. Introducing these values into Eq. 7, the S.F. of In^{III} from Ga^{III} is expressed as

Table 1. S_A and σ_A values

	S_A	σ_A
Ga^{III}	59.6	-36.8
In^{III}	50.9	-17.3

$$S.F. = -8.7S_{B} + 19.5\sigma_{B}. \qquad (8)$$

This equation may suggest that the contribution of soft factor of a chelating agent (σ_B) is more important for the separation than that of its hard factor (S_B). For the quantitative separation of In^{III} from Ga^{III}, the S.F. value should exceed 4.0. The application of this condition into Eq. 8 leads us to the following relationship:

$$\sigma_{B} \geq 0.21 + 0.45S_{B}. \qquad (9)$$

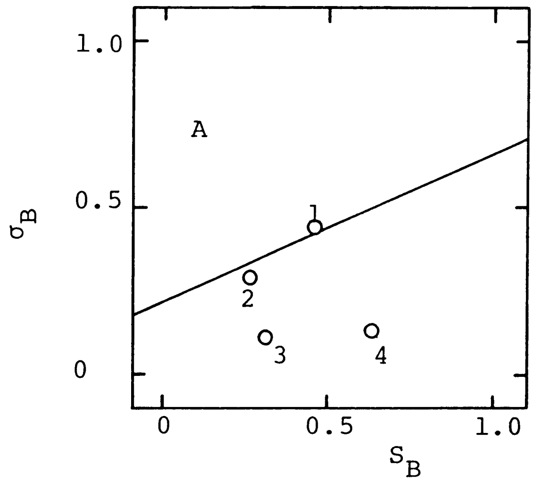
The values of σ_B and S_B for common chelating agents are given in Ref. 1. Then, a plot of σ_B against S_B based on Eq. 9 is shown in Fig. 1, where 8-quinolinol, TTA (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione), STTA (1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-butene-2-one) and dithizone (3-mercapto-1,5-diphenylformazan) are adopted as typical chelating agents. As seen in Fig. 1, only dithizone satisfies Eq. 9. The above predictions were confirmed though the experiments as follows:

Twenty cubic centimeters of an aqueous solution containing trace amounts of Ga^{III} or In^{III}, whose pH was preliminarily adjusted by adding nitric acid or sodium hydroxide, was placed in a separatory funnel. An equal volume of chloroform solution containing 5.0×10^{-3} M (M = mol dm^{-3}) chelating agent was added; the mixture was then shaken vigorously for 30 min. After the phases were allowed to separate, the pH of the aqueous phase was measured. To the organic phase 1 M nitric acid was added, and Ga^{III} or In^{III} was back-extracted into the aqueous phase, which was applied to inductively coupled plasma emission spectrometry to determine Ga^{III} or In^{III}. All experiments were carried out at room temperature (ca. 293 K).

The distribution ratio of metal(III) is defined as follows:

$$D = \frac{\text{The concentration of a metal in the } CHCl_3 \text{ phase}}{\text{The concentration of a metal in the aqueous phase}} . \quad (10)$$

The S.F. value obtained by the above experiments increased in the order of 8-quinolinol (S.F. = -3.4, pH = 2.0) < TTA (-0.9, 3.1) < STTA (2.1, 3.2) ≪ dithizone (>4, 2.6). The former three chelating agents are not effective for the separation. On the other hand, the quantitative separation of In^{III} from Ga^{III} with dithizone can be performed at the pH of ca. 2.6. Extraction curves for Ga^{III} and In^{III} with dithizone are given in Fig. 2.



A: A possible zone for the quantitative separation of In^{III} from Ga^{III}
1: Dithizone
2: STTA
3: TTA
4: 8-Quinolinol

Fig. 1. σ_B - S_B diagram.

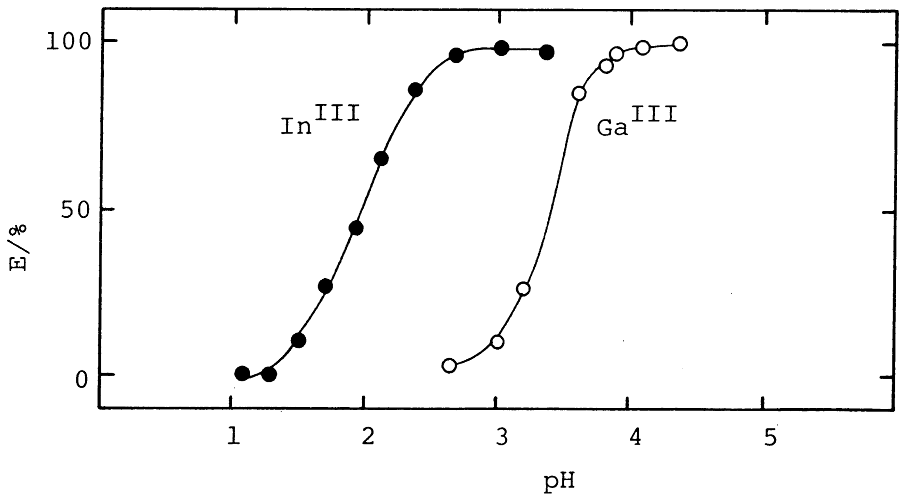


Fig. 2. Extraction curves.

All the above experimental results agree with the prediction, strongly suggesting that the design based on HSAB rule for the mutual separation of metal ions is practically effective. In addition, the present approach may help the molecular design of a future chelating agent on the basis of the values of S_B and σ_B.

References

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