Notes

Enhancement Effect of 3,5-Dichlorophenol on the Solvent Extraction of Scandium(III) with Acetylacetone

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The synergistic extraction of scandium(III) has been studied in a few systems of thenoyltrifluoroacetone and neutral electron donors, such as tributyl phosphate.^{1,2} These studies have shown that the enhancement effect of electron donors on the chelate extraction of scandium(III) is relatively small. We recently found that the extraction of iron(III) with acetylacetone (Hacac) is remarkably enhanced in the presence of a neutral proton donor, 3,5-dichlorophenol (DCP).³ It is very interesting to examine the effect of the proton donor on the chelate extraction of scandium(III).

In the present study, the extraction of scandium(III) with Hacac in heptane was investigated in the presence of DCP. The effect of DCP was quantitatively interpreted by analyzing the extraction equilibrium in detail.

the aqueous phase was adjusted with 1×10^{-4} – 1×10^{-3} M perchloric acid, acetic acid and sodium hydroxide solutions and measured with a glass electrode after shaking.

Results and Discussion

The extraction of scandium(III) with 0.010 M Hacac in either the absence or presence of 0.050 M DCP in heptane was carried out at various pH. The results are shown in Fig. 1. Although scandium(III) can not be extracted quantitatively with Hacac alone, the addition of 0.050 M DCP enhances the distribution ratio of scandium(III) by about 200-fold over the entire pH

Experimental

Reagents

A radioisotope ⁴⁶Sc, Hacac and heptane were either prepared or purified as described previously.⁴ DCP of 99% purity was purchased, and then further purified by vacuum sublimation. Water was doubly distilled. The other reagents were of analytical reagent grade and used as obtained.

Procedure

An aqueous solution containing 0.10 M sodium perchlorate and 1.0×10^{-5} M ($M = \text{mol dm}^{-3}$) scandium(III) labeled with ⁴⁶Sc was mechanically shaken with an equal volume of a heptane solution containing 5.1×10^{-3} – 5.1×10^{-2} M Hacac and 7.2×10^{-4} – 5.0×10^{-2} M DCP for 15–120 min at 25°C, and then centrifuged. The γ -activities of both phases were measured with a well-type NaI(Tl) scintillation counter and the distribution ratio (*D*) of scandium(III) was calculated. The pH value of

Fig. 1 Effect of DCP on the extraction of scandium(III) with Hacac in heptane. Initial composition of the organic phase: ● 1.0×10^{-2} M Hacac; ○ 1.0×10^{-2} M Hacac and 5.0×10^{-2} M DCP.

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region studied; the percent extraction reaches to 99% at pH 5. This effect of DCP is larger in magnitude than the enhancement effect of the neutral electron donors on the extraction of scandium(III) with thenoyltrifluoroacetone.^{1,2} It was confirmed that scandium(III) is not extracted at all with DCP alone.

Extraction equilibrium

The distribution ratio of scandium(III) with Hacac alone (D_0) can be expressed as

$$D_0 = \frac{[\text{Sc}(\text{acac})_3]}{[\text{Sc}^{3+}] + \sum_j [\text{Sc}(\text{acac})_j^{(3-j)+}]} \\ = P_M \beta_3 [\text{acac}^-]^3 (1 + \sum_j \beta_j [\text{acac}^-]^j)^{-1}, \quad (1)$$

where the bar denotes the organic phase, acac^- the acetylacetonate anion, P_M the partition coefficient of $\text{Sc}(\text{acac})_3$, and β_j the overall formation constant of $\text{Sc}(\text{acac})_j^{(3-j)+}$, respectively. These equilibrium constants were previously determined, i.e., $\log P_M = 1.041$, $\log \beta_1 = 8.02$, $\log \beta_2 = 14.38$, and $\log \beta_3 = 19.39$.⁴

In our previous studies, it was shown that $\text{Cr}(\text{acac})_3$ and $\text{Co}(\text{acac})_3$ form association complexes with halogenated phenols in nonpolar organic solvents by hydrogen bonding.^{5,6} The enhanced extraction of scandium(III) by DCP is therefore attributable to the association of $\text{Sc}(\text{acac})_3$ with DCP in the organic phase: the distribution ratio of scandium(III) with Hacac in the presence of DCP (D) can be expressed as

$$D = \frac{[\text{Sc}(\text{acac})_3] + \sum_n [\text{Sc}(\text{acac})_3 \cdot n\text{DCP}]}{[\text{Sc}^{3+}] + \sum_j [\text{Sc}(\text{acac})_j^{(3-j)+}]} \\ = D_0 (1 + \sum_n \beta_{\text{ass},n} [\overline{\text{DCP}}]^n), \quad (2)$$

where $\beta_{\text{ass},n}$ is the association constant in the organic phase, corresponding to the following equilibrium:

$$\beta_{\text{ass},n} = \frac{[\overline{\text{Sc}(\text{acac})_3 \cdot n\text{DCP}}]}{[\overline{\text{Sc}(\text{acac})_3}] [\overline{\text{DCP}}]^n}. \quad (4)$$

Therefore,

$$D/D_0 = 1 + \sum_n \beta_{\text{ass},n} [\overline{\text{DCP}}]^n. \quad (5)$$

The $\beta_{\text{ass},n}$ value can be determined based on Eq. (5) if reliable values of D_0 and the equilibrium DCP concentration in the organic phase ($[\overline{\text{DCP}}]$) are obtained. The estimation of D_0 and $[\overline{\text{DCP}}]$ should be made by considering the association between Hacac and DCP in the organic phase:

$$\beta_{\text{ass},i}^* = \frac{[\overline{\text{Hacac} \cdot i\text{DCP}}]}{[\overline{\text{Hacac}}] [\overline{\text{DCP}}]^i}, \quad (7)$$

where the association constant of Hacac with DCP, $\beta_{\text{ass},i}^*$, was previously determined, i.e., $\log \beta_{\text{ass},1}^* = 1.42$ and $\log \beta_{\text{ass},2}^* = 2.66$.³ The $[\overline{\text{DCP}}]$ and $[\overline{\text{Hacac}}]$ values were computed by solving the following simultaneous equations derived from the mass balances for Hacac and DCP:

$$C_{\text{AA}} = \{(1 + K_{\text{a,AA}}/[\text{H}^+])/P_{\text{AA}} + 1 + \beta_{\text{ass},1}^* [\overline{\text{DCP}}] + \beta_{\text{ass},2}^* [\overline{\text{DCP}}]^2\} [\overline{\text{Hacac}}] \quad (8)$$

and

$$C_{\text{CP}} = \{(1 + K_{\text{a,CP}}/[\text{H}^+])/P_{\text{CP}} + 1 + \beta_{\text{ass},1}^* [\overline{\text{Hacac}}] + 2\beta_{\text{ass},2}^* [\overline{\text{Hacac}}] [\overline{\text{DCP}}]\} [\overline{\text{DCP}}] \quad (9)$$

where C , P , and K_{a} denote the initial concentration, partition coefficient, and acid-dissociation constant, respectively, and subscripts AA and CP refer to Hacac and DCP. The literature values of P and K_{a} were adopted, i.e., $P_{\text{AA}} = 0.887$,⁷ $P_{\text{CP}} = 2.61$,⁸ $\text{p}K_{\text{a,AA}} = 8.82$,⁹ and $\text{p}K_{\text{a,CP}} = 8.25$.¹⁰ The D_0 value can be obtained from Eq. (1) using $[\text{acac}^-]$ calculated as $K_{\text{a,AA}} [\overline{\text{Hacac}}] P_{\text{AA}}^{-1} \times [\text{H}^+]^{-1}$.

Figure 2 shows a plot of $\log(D/D_0)$ vs. $\log[\overline{\text{DCP}}]$. The slope of the plot becomes close to the limiting value of 3.0 in the higher concentration region of DCP. This means that the maximum number of DCP molecules associated with one molecule of $\text{Sc}(\text{acac})_3$ is 3 under these

Fig. 2 D/D_0 as a function of the equilibrium DCP concentration in the organic phase. Initial composition of the organic phase: 5.1×10^{-3} – 5.1×10^{-2} M Hacac and 7.2×10^{-4} – 5.0×10^{-2} M DCP. Equilibrium pH: 2.8–3.9. D_0 and $[\overline{\text{DCP}}]$ values are calculated by considering the Hacac-DCP association (see the text). The solid line indicates the regression curve based on Eq. (5).

experimental conditions. The plot was treated by a nonlinear least-squares method (SALS program, The University of Tokyo) based on Eq. (5), and the association constants, $\log \beta_{\text{ass},1}=3.30\pm0.05$, $\log \beta_{\text{ass},2}=5.04\pm0.23$ and $\log \beta_{\text{ass},3}=7.16\pm0.08$, were obtained. These association constants are comparable to those of $\text{Fe}(\text{acac})_3$ with DCP in heptane, *i.e.*, $\log \beta_{\text{ass},1}=3.41$, $\log \beta_{\text{ass},2}=5.97$ and $\log \beta_{\text{ass},3}=7.50$.³

The $\beta_{\text{ass},1}$ of $\text{Sc}(\text{acac})_3$ with DCP is also comparable to the 1:1 adduct-formation constants of tris(thenoyltrifluoroacetato)scandium(III) ($\text{Sc}(\text{tta})_3$) with the neutral electron donors so far reported.^{1,2} However, $\text{Sc}(\text{acac})_3$ can form highly stable 1:2 and 1:3 association complexes with DCP, whereas $\text{Sc}(\text{tta})_3$ can only form the 1:1 adduct with the electron donors. Consequently, DCP can exert a larger enhancement effect on the chelate extraction of scandium(III) than the electron donors, thus enabling a sensitive extraction control by the concentration of DCP.

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