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## **Extractability of Lanthanoids(III) into Solvents Contributing to Environmental Protection**

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### **ABSTRACT**

To perform effective mutual separation of lanthanoids(III) by solvent extraction with avoiding several problems caused by diffusion of organic solvents into air and into water, into commercial available mixed solvents, aliphatic and aromatic solvents consisting of carbon number of 9 to 12, which have high boiling points or high flash points, the extraction of lanthanoid(III) thiocyanates with trioctylphosphine oxide has been measured and the equilibrium constants have been determined across lanthanoid series. Then the extraction constants were compared with those of single solvents, hexane and benzene, widely being used as solvents for liquid-liquid extraction.

The extraction constants obtained for the aliphatic mixed solvents are very similar to those for hexane across lanthanoid series. The variation of the constants for aromatic mixed solvents is also similar to that for benzene. The pattern of the variation of the distribution ratio under a constant condition across the series is similar to each other, either using the aliphatic solvents or using aromatic ones, except for in the middle of the series.

Accordingly, the use of the high molecular weight mixed aromatic solvents would be recommendable as organic solvents in the mutual separation of lanthanoids from the point of view of safety for fire and health for the people handling the extraction.

*Key Words: Separation Factors / Solvent Extraction / Rare Earths / TOPO / Organic Solvents*

### **INTRODUCTION**

There is no doubt that liquid-liquid extraction is one of the most useful techniques for the separation and recovery of metals in industrial scale as well as in laboratory scale. In solvent extraction, there are several serious economical and environmental problems caused by organic solvents, e.g., loss of solvents due to solubility in water, degradation, evaporation and adsorption, and toxicity. Year by year, much more attention has been paid from a viewpoint of environmental protection in a global scale as well as from that of the health of people handling solvents, and the restriction to use becomes more strict, e. g., the manufactures of carbon tetrachloride should be stopped in a near future.

In order to find out suitable organic solvents for both sides of the effective separation and environmental protection, the extraction of rare earths(III) with thiocyanate ions and trioctylphosphine oxide (TOPO) into mixed solvents of aromatic hydrocarbons as well as those of aliphatic ones consisting of C9-C12 has been examined, and the data was compared with those into hazardous solvents such as hexane<sup>(1)</sup> or benzene<sup>(2)</sup> which has been conventionally used in most solvent extractions.

## EXPERIMENTAL

**Reagents** All of the reagents were of analytical grade. Saturated aliphatic hydrocarbons and aromatic one were kindly supplied from Shell Japan Ltd. The commercial name of the aliphatic hydrocarbons was DOSB (the abbreviation to Deodorized Spray Base, and the number of carbon is 10 - 13, mainly it is consisted of C<sub>10</sub>H<sub>22</sub> and C<sub>12</sub>H<sub>26</sub>) and that of the aromatic solvent is Shellsol AB(C9 - C11, mainly C10 aromatic hydrocarbons, hereafter it is abbreviated as SSAB). They were shaken vigorously with 0.1M hydrochloric acid and rinsed with deionized water several times. Then the solvents were shaken with 0.1M sodium hydroxide solution and with deionized water to be neutralized. Other reagents were used without further purification. A sodium thiocyanate stock solution was prepared by weighting a portion of the saturated solution in the presence of the solid salt and by diluting it with deionized water. The concentration was determined by argentometry. Trioctylphosphine oxide (TOPO) was purchased from Dojindo Laboratories. Lanthanoid(III) stock solutions were prepared by dissolving the weighted oxide, which were obtained from Nakarai Tesque or Uldrich Japan, into hydrochloric acid. The exact concentration was determined by EDTA titration using Xylenol Orange as indicator.

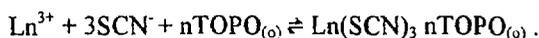
**Procedure** An aqueous solution consisting of Ln<sup>III</sup> and sodium thiocyanate solution of 1M (1 M = 1 mol dm<sup>-3</sup>) and an equal volume of an organic solvent containing various amounts of TOPO were shaken vigorously to attain the equilibrium. The pH was adjusted to 4. The concentration of lanthanoid(III) distributed between the two phases was determined as follows: the metal(III) in the organic phases was determined after back extraction into 10<sup>-2</sup>M perchloric acid, and that in the aqueous phases after diluting with 10<sup>-2</sup>M perchloric acid as much as 10 times was determined by ICP-AES, respectively. When the extractability is low, the concentration in the aqueous phases was represented as the balance between the initial concentration and the concentration in the organic phases at equilibrium. The concentration ratio between both phases was defined as the distribution ratio, D.

## RESULTS AND DISCUSSION

1) **Determination of extraction constants** Figure 1 depicts the distribution ratio of lanthanoids(III) as a function of the total TOPO concentration when lanthanoids(III) (the total metal concentration, M<sub>T</sub> = 5x10<sup>-4</sup>M in Fig. 1-a, and M<sub>T</sub> = 6x10<sup>-4</sup>M except for lanthanum(III), 8.5x10<sup>-4</sup>M in Fig. 1-b) were extracted from 1M sodium thiocyanate solution. The extraction of lanthanoids(III) into the aliphatic mixed solvent is more similar to each other than that into aromatic one, e.g., the distribution ratio at 10<sup>-3</sup>M TOPO across lanthanoid series is ranged only in 0.1 to 1 using aliphatic solvent(Fig. 1-a), while that is from 0.002 to 0.5 using the aromatic solvent(Fig.1-b). Figure 1 also shows that the slope of the extraction curves for light lanthanoids(III), e.g., La<sup>III</sup>, is larger than that for heavy ones, e.g., Lu<sup>III</sup>, and the slope of a extraction curve seems to change depending on TOPO concentration. Such a trend suggests that the extraction behavior into these commercial mixed solvents is similar to that into regular solvents such as hexane and benzene(1,2). The distribution ratio can be related to TOPO concentration at equilibrium as,

$$D = \frac{\sum K_{exn} [E]_o^n [X^-]^3}{1 + \beta_1 [X^-]} \quad (1)$$

where K<sub>exn</sub> are the equilibrium constants in the following extraction equilibrium,



and β<sub>1</sub> is the stability constant of the first thiocyanate complex in the aqueous solution<sup>(2)</sup> represented by

$$\beta_1 = [\text{Ln}(\text{SCN})^{2+}] / ([\text{Ln}^{3+}][\text{SCN}^-])$$

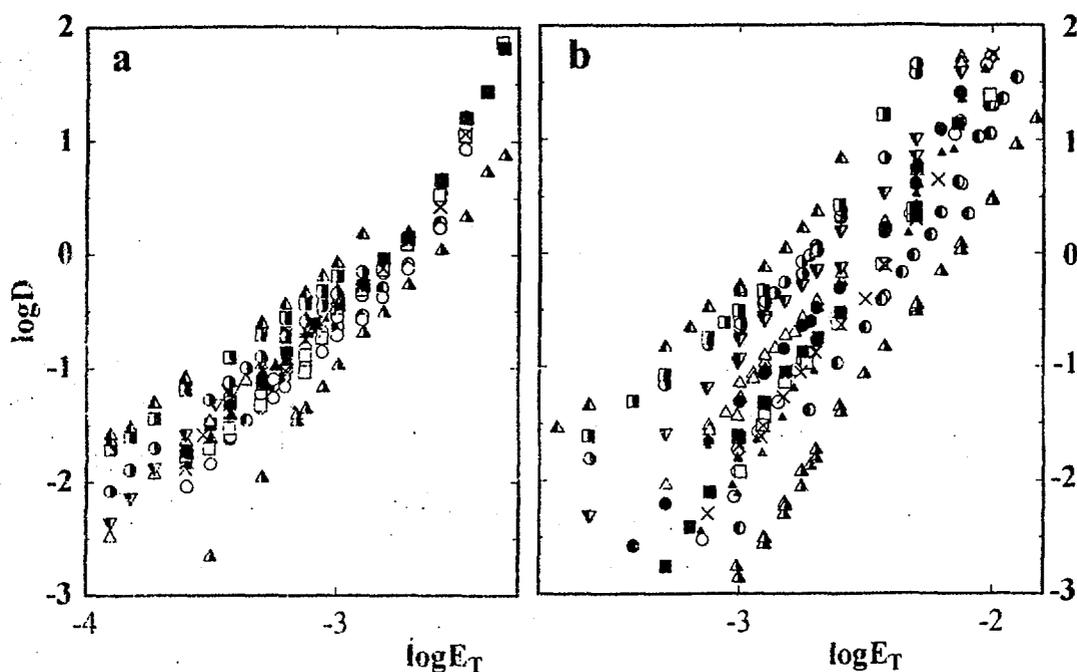


Fig. 1. Distribution ratio of  $\text{Ln}^{\text{III}}$  against the total TOPO concentration, when  $\text{Ln}^{\text{III}}$  ( $M_T = 5 \times 10^{-4} \text{M}$  for a and  $6 \times 10^{-4} \text{M}$  except for La ( $8.5 \times 10^{-4} \text{M}$ ) for b) is extracted into DOSB(a) and SSAB(b).

La(▲) Pr(●) Nd(○) Sm(▲) Eu(□) Gd(×) Tb(■)  
 Dy(△) Ho(●) Er(▽) Tm(○) Yb(■) Lu(▲)

When the extractability is very poor, the TOPO concentration at equilibrium,  $[E]_o$ , can be regarded as the total concentration,  $E_T$ . However, since with increasing of the extractability, the TOPO concentration at equilibrium is going to be smaller than the total concentration, because metal(III) molecule is extracted with accompanying several TOPO molecules.

Then the total TOPO concentration can be related to the TOPO concentration at equilibrium as,

$$E_T = [E]_o + \frac{M_T \sum n K_{ex_n} [E]_o^n [X^-]^3}{1 + \beta_1 [X^-] + \sum K_{ex_n} [E]_o^n [X^-]^3} \quad (2)$$

In the present study,  $[X^-]$  is 1.0M, and it is a large excess of the extracted lanthanoid(III) concentration. As mentioned above, the extraction behavior into the mixed solvents is very similar to that into hexane or benzene so that 3 and 4 were assumed as  $n$  similarly in the analysis of the data for these conventional solvents, and the data in Fig. 1 were analyzed according to Eqs. (1) and (2). The calculation was repeated until all points in the data were explained using the extraction constants.

The constants obtained are listed in Table 1. In Fig. 2 the constants obtained in the present study are compared with those using hexane and benzene. The pattern of the variation of the extraction constants,  $K_{ex_3}$  as well as  $K_{ex_4}$ , across the lanthanoid series is similar to each other, i.e., either between aromatic and aliphatic solvents, or between the single and the mixed solvents. Especially, the values of the extraction constants are very similar across lanthanoid series between hexane and the mixed aliphatic hydrocarbons. In more detail, the difference between  $\log K_{ex_4}$  and  $\log K_{ex_3}$  is a little larger in the aliphatic solvents than in the aromatic ones, i.e., in aliphatic solvents the main extracted species are

Table 1 The extraction constants of lanthanoids(III) as thiocyanates with TOPO into aliphatic and aromatic mixed solvents (C9 - C12) at 298K. (\* Ref. 1)

solvent		aliphatic		aromatic	
Ln <sup>III</sup>	logβ <sub>1</sub> *	logK <sub>ex3</sub>	logK <sub>ex4</sub>	logK <sub>ex3</sub>	logK <sub>ex4</sub>
La	0.14	-	11.7	-	9.4
Pr	0.34	-	12.7	-	10.1
Nd	0.43	-	13.0	-	10.75
Sm	0.34	-	13.2	-	10.6
Eu	0.35	-	13.1	-	11.0
Gd	0.40	9.5	12.7	-	10.75
Tb	0.44	9.7	12.7	-	11.0
Dy	0.45	9.7	13.4	8.3	11.1
Ho	0.45	9.2	13.4	8.3	10.8
Er	0.45	9.8	13.4	9.0	-
Tm	0.42	10.1	-	9.5	-
Yb	0.41	10.5	-	9.8	-
Lu	0.45	11.1	-	10.4	-

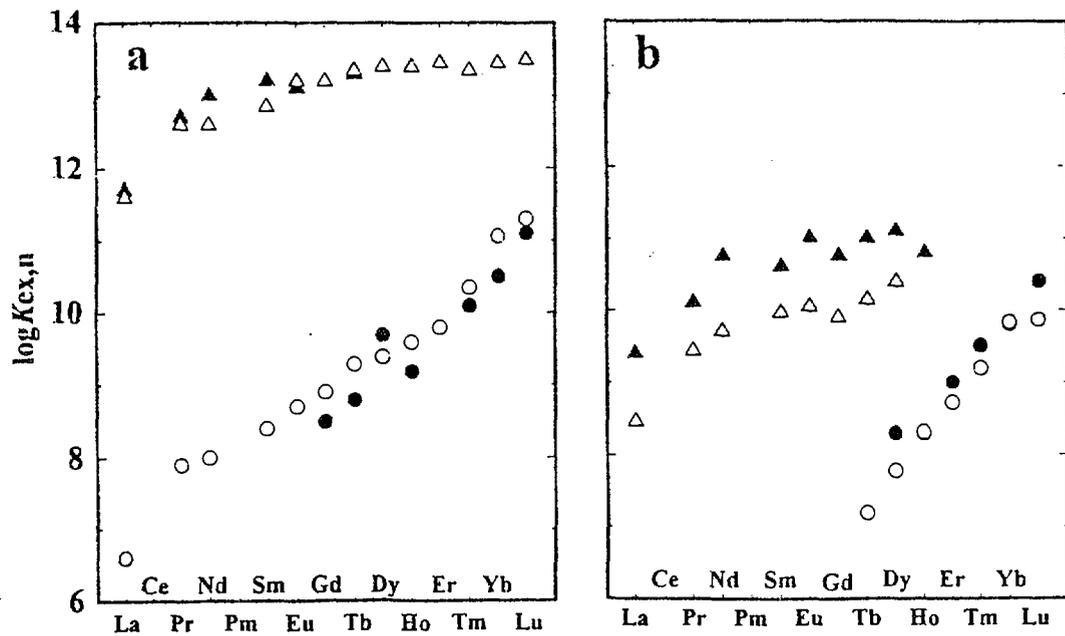


Fig. 2. Comparison of extraction constants (\*1 Ref. 1 \*2 Ref. 2)

a : Extraction into aliphatic solvents(closed symbols DOSB open symbols hexane<sup>\*1</sup>)  
 b : Extraction into aromatic solvents(closed symbols SSAB open symbols benzene<sup>\*2</sup>)  
 circles : log K<sub>ex3</sub> triangles : log K<sub>ex4</sub>

$$K_{exn} = \frac{[LnX_3nE]_o}{[Ln^{3+}][X^-]^3[E]_o^n}$$

accompanied with 4 TOPO molecules. The difference of  $K_{ex4}$  across the series is smaller than that of  $K_{ex3}$ . These observations may suggest that since the solvent-solute interaction as well as the solvent-solvent interaction is weaker in aliphatic solvents than that in aromatic ones, the higher complexes with TOPO can be extracted, and also the lower complexes should give the metal proper nature. From such a trend, it may be expected that the larger separation factor between the adjacent lanthanoids would be obtained by using aromatic solvents than aliphatic ones.

2) **Comparison of the separation factors using aliphatic solvents and aromatic ones.** Figure 3 shows the distribution ratio when lanthanoids(III) are extracted under a given condition. The variation of the distribution ratio across lanthanoid series represented by open circles is smaller than that by closed circles, although both the extraction is carried out using a similar TOPO concentration (in the former  $E_T = 1.0 \times 10^{-3} M$  and in the latter  $E_T = 1.25 \times 10^{-3} M$ ). The difference of the pattern can be explained as follows: since in the former the concentration of  $M_T (5 \times 10^{-4} M)$  as well as  $E_T$  is kept constant, TOPO concentration at equilibrium in the extraction of heavier lanthanoids(III) is lower than that of lighter ones, because the larger number of TOPO molecules would be trapped with the extracted heavier lanthanoids(III) for the better extraction, e.g.,  $\log[E]_o$  is -3.1 for La but -3.5 for Lu, while since in the latter, TOPO concentration at equilibrium is kept constant ( $\log[E]_o$  is almost -3.1 which is controlled with changing the initial lanthanoid(III) concentration, e.g.,  $M_T$  is  $4.3 \times 10^{-4} M$  for La and  $1.5 \times 10^{-4} M$  for Lu), the distribution ratio varies as expected from the extraction constants.

For the mutual separation of metals, we should compare among the extractabilities at an identical

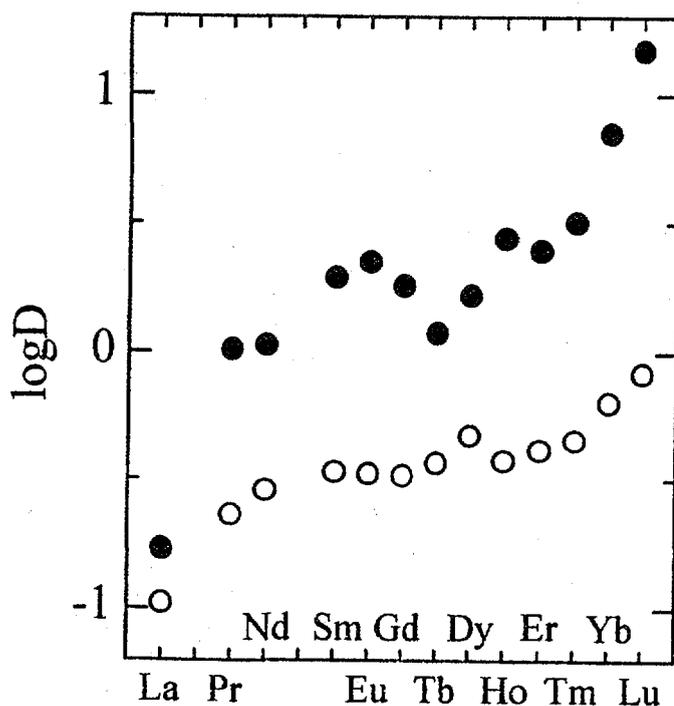


Fig. 3. Variation of  $\log D$  across lanthanoid series when  $Ln^{III}$  is extracted under a constant condition.

Aq. phase	1M NaSCN	Organic solvent	DOSB containing TOPO
●	$E_T = 1.25 \times 10^{-3} M$	$[E]_o = 1 \times 10^{-3} M$	$M_T$ varied
○	$E_T = 1.0 \times 10^{-3} M$	$M_T = 5.0 \times 10^{-4} M$	$[E]_o$ varied

extractant concentration at equilibria. Figure 4 shows the distribution ratio obtained by using the aliphatic solvent, DOSB( $\circ$ ) and Isopar G, Exxon Chemical, C10 - C11; ( $\bullet$ ) at a constant extractant concentration;  $E_T = 1.8 \times 10^{-3} M$  and  $[E]_0 = 7.4 \times 10^{-4} M$ , changing the initial lanthanoid(III) concentration (e.g.,  $8.5 \times 10^{-3} M$ (Pr) and  $3.5 \times 10^{-4} M$ (Lu)). The values of  $D$  do not seem to depend on companies manufactured. As mentioned above, the values of the extraction constants obtained either for hexane or for DOSB are very similar to each other. Accordingly, it may suggest that the extractability of a  $Ln(SCN)_3$  with TOPO into any aliphatic solvents is very similar.

Figure 4 also shows the distribution ratio obtained using SSAB( $\triangle$ ) and Solvesso 150 (Exxon Chemicals, C10-C11 aromatic solvent;  $\blacktriangle$ ). The  $E_T$  and  $[E]_0$  are also kept constant,  $2.5 \times 10^{-3} M$  and  $1.5 \times 10^{-3} M$ , respectively. The total metal concentration  $M_T$  is varied from  $0.01 M$ (Pr) to  $4 \times 10^{-4} M$ (Lu). Although the extraction constants are a little different between SSAB and benzene as shown in Fig. 2, the difference of the distribution ratio is not observed between SSAB and Solvesso 150. It may be due to the number of carbons.

As seen from Fig. 4, the difference of the distribution ratio between adjacent lanthanoids, so called the separation factor, does not seem to be observed among the light lanthanoids, either using the aliphatic mixed solvents or the aromatic ones. However among from Gd to Tm, a little larger separation factor is observed using the aromatic solvents, reflecting the smaller difference between  $\log K_{ex4}$  and  $\log K_{ex3}$  for the aromatic solvents.

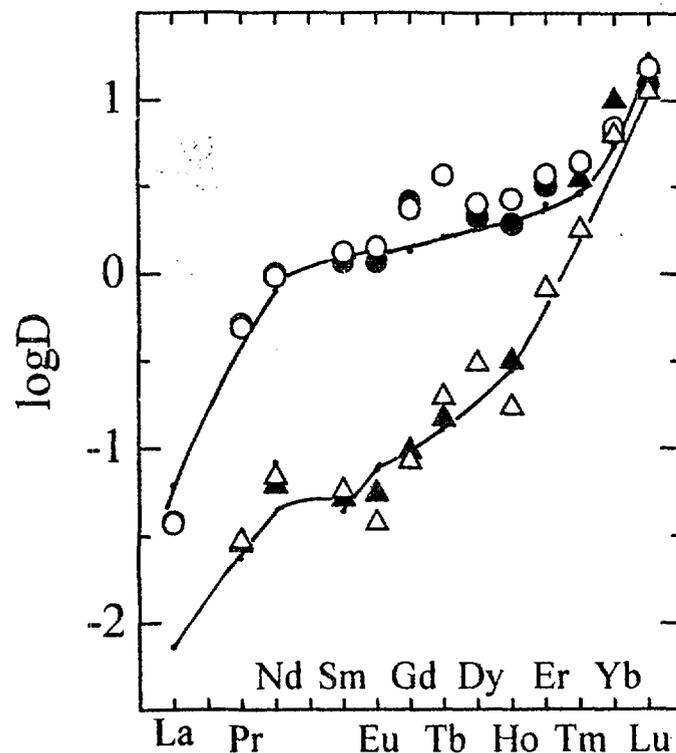


Fig. 4. Variation of  $\log D$  across lanthanoid series under a constant condition  
 Aq. phase  $1 M NaSCN$  and  $Ln^{III}$   
 Org. phase DOSB( $\circ$ ) and ISOPAR G( $\bullet$ ) at  $E_T = 1.8 \times 10^{-3} M$   $\log[E]_0 = -3.1$   
 SSAB( $\triangle$ ) and Solvesso 150( $\blacktriangle$ ) at  $E_T = 2.5 \times 10^{-3} M$   $\log[E]_0 = -2.9 \sim -3.0$   
 Solid curves represent the distribution ratio calculated according to Eq. (1) using the extraction constants.

Table 2 Several properties of organic solvents

solvents	flash point/°C	bp/°C	density	remarks
C <sub>6</sub> H <sub>14</sub>	-26	69	0.659	very volatile (narcotic)
DOSB	45	182~290	0.746	aliphatic hydrocarbon mixture of C <sub>10</sub> H <sub>22</sub> and C <sub>12</sub> H <sub>26</sub> >98.0wt% nonvolatile
C <sub>6</sub> H <sub>6</sub>	-11	80	0.874	highly flammable, toxic (carcinogen)
SSAB	65	187	0.896	aromatic hydrocarbons >84.4wt% C10

3) Choice of organic solvents to contribute to environmental protection. Table 2 shows the properties of respective solvents. As seen from Table 2, the flash points as well as boiling points of the commercially available solvents studied in the present work, either aliphatic mixed solvents or aromatic ones, are much higher than hazardous single solvents which are conventionally used in solvent extraction. In addition, the solubility of these mixed solvents in water should be much less than that of the conventionally used single solvents, due to the higher molecular volume. The less loss of the solvents into air and water would be effective economically and also environmentally. In the present study, the mixed solvents consisting of C9 to C12 are used. If the higher molecular weight hydrocarbons are used as organic solvents, the less loss should be expected. However, since the viscosity also increase with increasing the number of carbons, other problems such as difficulty of the phase separation and bothering to clean vessels may come out. The solvents studied in the present work may be most effective.

## CONCLUSION

From the present results it has been found that the extraction behavior of lanthanoid(III) thiocyanates with TOPO into mixed hydrocarbons consisting of C9 - C12 is very similar to that into single solvents, although the proportion of the composition is not uniform, and also the separation factor is larger on using aromatic solvents than aliphatic ones. Since hydrocarbons of the higher molecular weight would have higher boiling points, higher flash points, and the less solubility in water, the use of the aromatic hydrocarbons in the vicinity of C10 may be recommendable as a solvent which contributes to environmental protection, in the mutual separation of lanthanoids(III) at least with the ion-association extraction.

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