Synergistic Effect in the Solvent Extraction of Trivalent Lanthanides by Neutral Phosphine Oxides

By C. T. Rhee

Atomic Energy Research Institute, Korea

三價稀土類元素의 溶媒抽出上의 相乘效果

李　　鎭　　澤*

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Abstract

Synergistic effect was observed in the extraction of trivalent lanthanides by the mixed solvent of TBPO (tri-n-butyl phosphine oxide) and TOPO (tri-n-octyl phosphine oxide) in toluene diluent. The reason of the enhancement was verified as mainly due to the formation of new extractable species $M(NO_3)_3(TBPO)_2$ $(TOPO)$ besides of the formation of $M(NO_3)_3(TBPO)_3$ and $M(NO_3)_3(TOPO)_3$.

要　　約

TBPO와 TOPO와의 混合溶媒(稀釋劑 : toluene)에 依한 三價狀態의 4f 稀土類元素의 抽出에있어 相乘效果 (synergistic effect)가 나타남을 알았으며 이것은 各 單獨溶媒系에 있어서 生成抽出되는 $M(NO_3)_3$ $(TBPO)_3$ 및 $M(NO_3)_3$ $(TOPO)_3$型 外에 $M(NO_3)_3$ $(TBPO)_2$ $(TOPO)$型이 새로히 追加生成됨에 起因된 것으로 認定된다.

Introduction

Since the word "synergism" was first coined by Baes et al., [1] to describe their discovery of a definite enhancement of the extraction of uranium by a mixture of an acidic dialkyl phosphate and certain neutral organic phosphorus esters, many works have been reported for the extraction of metallic ions by mixed solvents. Blake et al considered that this synergistic enhancement seemed to be limited in their experiments to dialkyl phosphoric acid-neutral reagent combinations and that, out of several elements studied, U(VI) was the only one which extracted synergistically. A few years prior to the above work Cunningham et al. [2] at Harwell reported that mixtures of TTA (thenoyl trifluoroacetone) and TBP (tri-butyl phosphate) in ben-zene diluent would extract Pr and Nd to a greater extent than either reagent alone.

There are many works reported other than above mentioned with neutral organic phosphorus esters, $(R_3PO_4, R_3PO_3, R_3PO_2, R_3PO)$ combined with dialkyl phosphoric acid, [3,4,5,6,18] monoalkyl phosphoric acid, [3,7,8] phosphinic acid, [1,3] an dwith TTA[8,9,10,11,14] [15,16,17,20]. The other systems studied are dialkyl phosphoric acid with amines (primary, secondary, tertiary), [3,12] with hexol[19], monoalkyl phosphoric acid with n-decyl alcohol[7,8].

For the system of none phosphorus compounds, A. G. Maddock et al. [13] reported some synergism for Pa(V) by di-isopropyl carbinol mixed with various organic compounds — di-isobutyl ketone, nitro methane, benzonitril, nitrobenzene, di-chloro diethyl ether, di-isopropyl ether or acetophenone. Some of workers described their discovery of a definite decrease of the extraction of metal ions by a mixture of solvents and named this phenomena as antiergism [9,13] or negative

synergism[7].

As a general tendency of positive synergism the curves of distribution ratio showes a maximum value and after that point the curves turn to decrease according to the mixing ratio of two solvents. Even though there has been no general explanation for the mechanism of synergism established so far, many clear approaches were achieved case by case. Among the various approaches (I) some displacement of the first solvent by the second one in the extracted species, [2] [4] (II) further addition of the second solvent to the extracted species through coordination number change or hydrogen bonding,[1) 3) 5)] (III) displacement of the hydrated water molecule by the second solvent in the extracted species, [9) 8) 10) 11) 20)] and (IV) change of the characteristics of organic phase by the addition of second solvent such as dielectric constant and positive deviation from Raults law [(10) (11) (13)] were the typical considerations. For the negative synergism and also the negative slope of the synergistic curve after maximum point were explained as the increasing interaction with second solvent resulting formation of less or none active solvent species according to the increasing of mixing ratio. [7) 4)] The auther decided to examine the mixed system of TOPO (tri-n-octyl phosphine oxide) and TBPO (tri-n-butyl phosphine oxide) for the extraction of trivalent lanthanides from aqueous nitrate solution since there has been no published work so far for such mixed neutral organic phosphorus solvents. From this study some definite synergistic effect was observed and the extracted species by the mixed system were confirmed as M(TBPO)$_2$(TOPO)(NO$_3$)$_3$.

Experimental

Sources of materials

TBPO was received from Tama Chem. Co., Japan and was used without further purification. This was stored in the refrigerator. TOPO received from Eastman Chemicals Co., U. S. A. was also used without further purification because the melting point measurement of this same reagent by Japan Atomic Energy Research Institute showed the values of ∼60°C ensuring that the purity was satisfactorily high. C. P. grade TBP received from J. T. Baker Chemical

Co., U. S. A. was further purified in a manner similar to that used by Pepperd et al. [21) 22)] Toluene, Cyclohexane and Chloroform supplied by E. Merck, Germany were analytical grade. Other chemicals used were all C. P. grade.

2. 6 year Pm[127], 127 d Tm[170] and (13, 16) year Eu[152, 154)] were obtained Raio Chemical Center, England.

Beckman model IR-4 infrared spectrometer was used for spectroscopic analysis.

Determination of distribution ratios

The distribution ratio, K_d, for a given nuclides was obtained radiometrically by allowing the nuclides to reach a distributing equilibrium, between the two mutually equilibrated liquid phase, and then determining the radioactivity of aliquot of each phase using NaI(Tl) well type scintillation counter. Equilibrium distribution of radionuclides was accomplished by four min. manual shaking in a glass stoppered 5ml measuring cylinder. Pre-equilibriation was made by changing the aqueous phase.

Results and discussion

The similarity between TOPO and TBPO in the extraction of same nuclide is not hard to predict. The plots of the distribution ratio. Kd, for Pm and Eu vs. the concentration of TOPO and TBPO at 0.25N nitric acid are shown in Fig. 1, Fig. 2 shows the same plots for Pm and Tm at 1 N nitric acid. These plots shows essentially the same slope without regarding the species of nuclides in the rare earth series and the value is 2.6∼2.7. The Kd value of Eu is higher than either that of Pm or Tm. This results make to predict non monotonic ordering of lanthanides extraction by TBPO or TOPO as the case of TBP.[22)] And also TBPO has somewhat stronger extraction ability than TOPO. This can be explained by the stronger basicity and/or by the smaller moleculer size. It was already pointed out[23)] that the complexed TOPO with nitric acid does not extract nuclide and explained the maximum Kd value occuring at 0.25N nitric acid for the extraction of trivalent lanthanides from nitric acid solution by TOPO.

The variation of Kd value of Pm by 2%(W/V) TBPO in toluene as a function of nitic acid concentration is shown in Fig.3. The curve shows maximum value at around 0.25N nitric acid as is the case
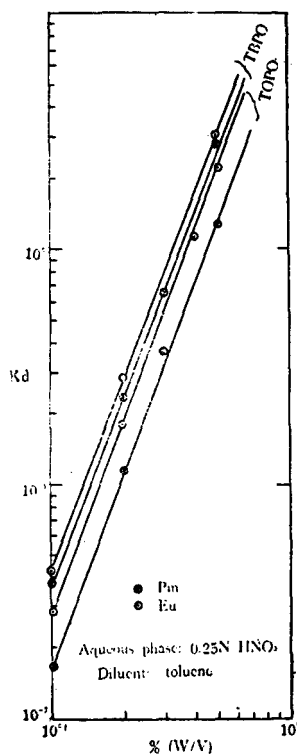
Fig.1 Variation of Kd of Pm and Tm as a function of the concn. of TBPO.
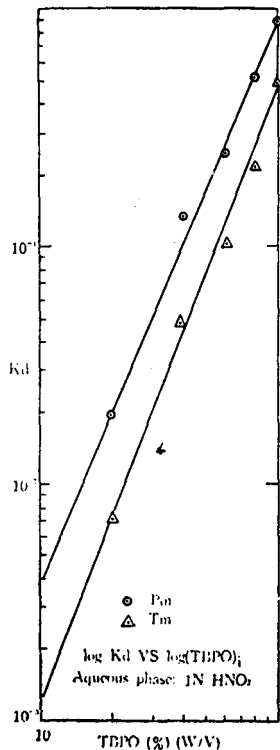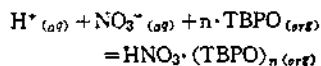

Fig.2 Variation of Kd value as a function of the concn. of TBPO & TOPO

of TOPO.

Since there is no reported value of the equilibrium quitient for the reaction:

$$H^+_{(aq)} + NO_3^-_{(aq)} + n \cdot TBPO_{(org)}$$
$$= HNO_3 \cdot (TBPO)_{n \, (org)}$$

it is hard to calculate the concentration of effective TBPO, $TBPO_{eff}$, which is actually participate in extracting nuclide, it is expected to be nearly same value as the case of TOPO considering the very similar value and slope of the curves in Fig. 1 and 2 which are plotted against initial concentration of TBPO and TOPO, $TBPO_i$ and $TOPO_i$. Zingaro et al.[24] calculated the value of K as 9.1 for TOPO. The variation of Kd value for Tm as a function of nitric acid at 1M constant ionic strength of nitrate ion using ammonium nitrate as salting agent is shown in Fig. 4. As already pointed out [23] the value of log $\{Kd/(TBPO)^m_{eff}\}$ should be constant under the condition of constant

nitrate ion concentration. [*]

Supposing the value of K' as 9 for the convenient, the variation of $Kd/(TBPO)^m_{eff}$ as a function of m are shown in Fig. 5 using the value of Kd on Fig. 4. Among the three curves, the curve of m=3 shows fairly good fit to constant value.

From these facts the form of extracted species of trivalent lauthanides by TBPO

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[*] [The extraction of trivalent lant-hanide can be written as

$$M^{+3}_{(aq)} + 3NO_3^-_{(aq)} + m \cdot TBPO_{(org)}$$
$$= M(NO_3)_3(TBPO)_{m \, (org)}$$
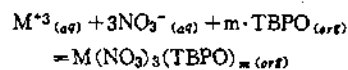
$$K_d = \frac{M(NO_3)_3(TBPO)_{m \, (org)}}{(M^{+3})_{(aq)}}$$

$$K' = \frac{M(NO_3)_3(TBPO)_{m \, (org)}}{(M^{+3})_{aq}(NO_3^-)^3_{(aq)} \cdot (TBPO)^m_{(org)}}$$

from these two equations

$$\log K_d = 3\log(NO_3^-)_{aq} + \log K'(TBPO)^m_{(org)}$$

$$\log\{kd/(TBPO)^m_{org}\} = 3 \, \log(NO_3^-)_{aq} + \log K'$$
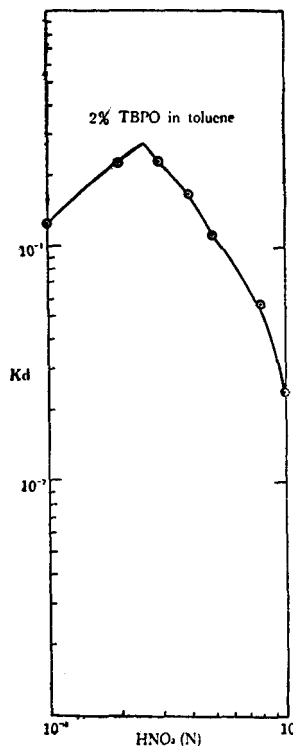
here $TBPO_{org} = TBPO_{eff}$.]

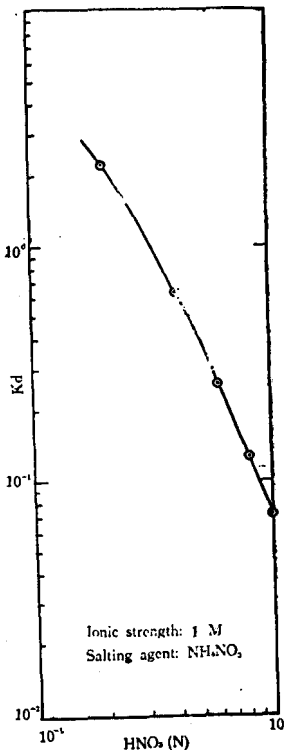**Fig.3** Variation of Kd value of Pm as a function of (HNO₃)

Fig.4 Variation of Kd value for Tm as a function of (H⁺)aq. at 1M (NO₃⁻)aq.

from nitrate solution can be considered as $M(TBPO)_3$ $(NO_3)_3$ which is exactly the same form of $M(TOPO)_3(NO_3)_3$ in the case of TOPO.

The variation of Kd value of Pm and Eu as a function of TBPO and TOPO concentration and as a function of each at 0.25N nitric acid are shown in Fig 6 and 7. If there is no synergistic effect, the solid line should be essentially overlapped to the chained line which is drawn by arithmatical addition of each dotted line. These results shows that, even though the enhancement is not significant compared with the
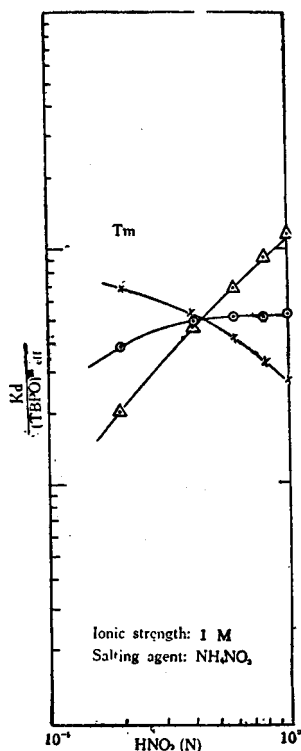

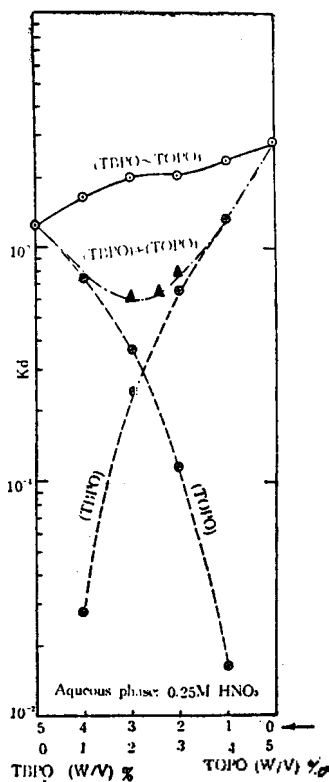**Fig. 5** Variation of $(H^+)aq$. independency of $Kd/(TBPO)^*_{ork}$ for various m.

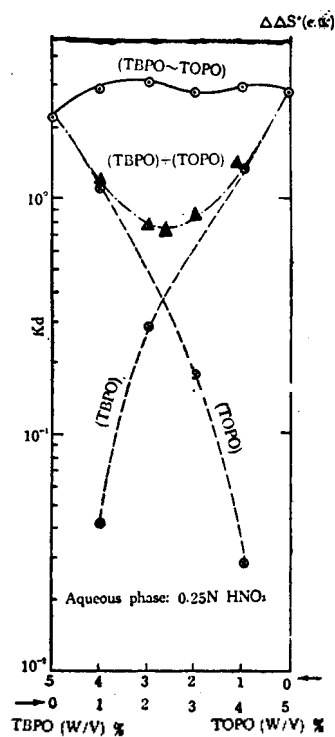**Fig. 6** Synergistic effect in the extraction of Pm by TBPO & TOPO in toluene

Fig. 7 Synergistic effect in the extraction of Eu by TBPO in toluene

case of mixing acidic and neutral solvent which reached $\sim 10^4$ order for particular case[9], the distribution ratio by the present mixed solvent is generally a few times larger than the additional value of each solvent alone.

Since the order of enhancement is so small it is reasonably possible to consider that such enhancement might be derived from the possible change of some characteristics in the solvent phase as was suggested by A. G. Maddock et al[13]. As is known, the extraction power with same solvent is decreased in the order of innert diluent: cyclohexane > hexane > CCl₄ > benzene > CHCl₃. These are the same order of their

polarity and toluene used in this experiment should has a position between cyclohexane and chloroform. Table I shows the results of the variation of synergistic effect for Tm according to the variation of diluent. As was expected, the Kd value for the system of toluene diluent is much larger than that of chloroform diluent and smaller than that of cyclohexane diluent. But the synergistic effect for toluene system is larger than either of cyclohexane or chloroform system. If the addition of TOPO or TBPO to the TBPO or TOPO phase respectively cause all or some part of the enhancement in the extraction, the resulted synergistic effect shown in Table I should

not be that sequence.

Table I. Variation of synergistic effect for Tm according to diluent

Solvent	Diluent	Kd	Synergistic effect Kd_{1-2} /$Kd_1 + Kd_2$
2% TBPO	Toluene	5.23×10^{-2}	
2% TOPO	Toluene	1.81×10^{-2}	
2% TBPO TOPO	Toluene	1.97×10^{-1}	~2.8
2% TBPO	Cyclohexane	3.35×10^{-2}	
2% TOPO	Cyclohexane	1.46×10^{-1}	
2% TBPO TOPO	Cyclohexane	4.47×10^{-1}	~2.5
2% TBPO	Chloroform	$5.3_- \times 10^{-4}$	
2% TOPO	Chloroform	9.26×10^{-4}	
2% TBPO TOPO	Chloroform	1.59×10^{-3}	~1.1

Fig. 8 shows the variation of synergistic effect in the extraction of Pm by TBPO and TOPO in toluene as a function of nitric acid. The synergistic effect in the right part is somewhat larger than the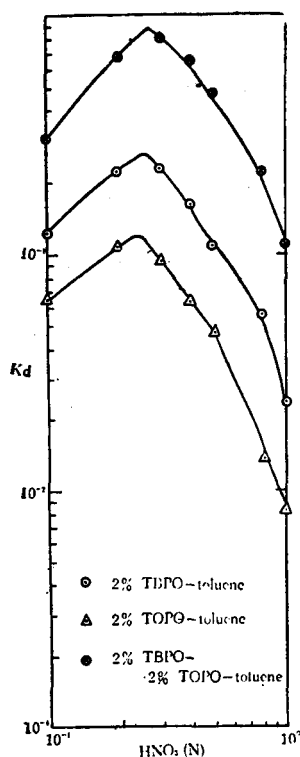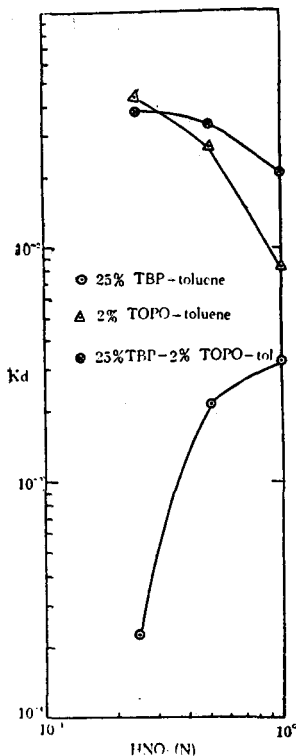 left part Fig. 9 shows the variation of Kd value of Tm for the system of 25% (v/v) TBP-tol., 2% (w/v) TOPO-tol. and 25%(v/v) TBP-2%(w/v)T-OPO-tol. as a function of nitric acid. The two curves of TOPO and TBP-TOPO in Fig. 9 are crossed each other at the acidity of ~0.3N nitric acid. This results can be well explained from the possible decreasing of the concentration of nitric acid by TBP. The same consideration can be applied to explain the difference of the synergistic effects between right and left side in Fig. 8.

There was no positive evidence for the possible interaction between TBPO and TOPO in toluene from the results of infrared spectroscopy. If the synergistic effect is resulted from the formation of new species, the overall distribution ratio, Kd_{total}, can be expressed as; $Kd_{(total)} =$

$$\frac{M(NO_3)_3 (TOPO)_{3 \, org} + M(NO_3)_3(TBPO)_{3 \, org} + M(NO_3)_3(TBPO)_x(TOPO)_y}{M_{aq}}$$

$$Kd_{(total)} = Kd_{(TOPO)} + Kd_{(TBPO)} + \Delta Kd$$

where $Kd_{(TOPO)}$ and $Kd_{(TBPO)}$ are the extraction

Fig. 8 Synergistic effect in the extraction of Pm by TBPO & TOPO in toluene as a function of (HNO₃).

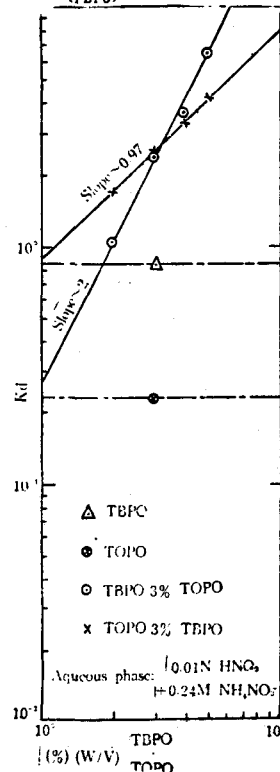**Fig. 9** Variation of Kd value of Tm as a function of TBP & TOPO.

Fig. 10 Kd Value of Tm for mixed solvent providing the concn. of one component be fixed.

ratio expected for each reagent alone.

The magnitude of the increase in extraction, ΔKd, is determined by the formation constant,

$$K_{mix} = \frac{M(NO_3)_3(TBPO)_x(TOPO)_y \, org}{(TBPO)^x(TOPO)^y M_{aq}(NO_3)^3_{aq}}$$

$$\Delta Kd = K_{mix}(TBPO)^x(TOPO)^y(NO_3)^3$$

and

$$\left(\frac{\delta\log\Delta Kd}{\delta\log(TBPO)}\right)(TOPO)(NO_3)$$

$$= x : \left(\frac{\delta\log\Delta Kd}{\delta\log(TOPO)}\right)(TBPO)(NO_3) = y$$

Fig. 10 shows the variation of Kd values of Tm for the mixed system of TBPO and TOPO providing the concentration of one component is fixed to 3% (w/v) each other. The concentration of nitrate ion was kept to 0.25M by adding ammonium nitrate to the 0.01 N nitric acid solution. With this condition, the non active complexed solvent with nitric acid should be expected to be negligible. The slope of the curve of TBPO-3% TOPO is ~2 and that of TOPO-3% TBPO is ~0.97. Thus, it is concluded that the synergistic enhancement in the extraction of trivalent lanthanides by the mixed solvent of TBPO and TOPO in toluene due to mainly formation of a new extractable species of $M(NO_3)_3(TBPO)_2(TOPO)$ (here the some possible hydrated water molecule was not considered) and this mixed complex is more stable than either of $M(NO_3)_3(TBPO)_3$ or $M(TOPO)_3(NO_3)_3$ in toluene diluent.

Acknowledgement

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