Extraction Rate and Temperature Dependency of Distribution Ratio of 4f and 5f Series Element in the Various Phosphorus Compounds

by

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各種 燐化合物溶媒 抽出系에 있어서 4f 및 5f 系列 元素의 抽出速度 및 分配率의 溫度依存性

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ABSTRACTS

The distribution rate of 4f and 5f series elements in chelate and ion association extraction system was studied.

Clear difference between lighter and heavier part of 4f series are observed. Trivalent Am and Cm were appeared to be grouped into the lighter part of 4f series. And also the variation of distribution ratio according to the varied temperature was studied. The variation modes of distribution ratio are different according to the extraction system. Atomic number dependence in the chelate extraction system was observed.

INTRODUCTION

The rate of extraction depends on two factors; namely, the formation rate of extractable chemical species and the transferring rate of the species from one phase to the other. But it is generally understood that the second factor(transferring rate) does not make much difference for similar extraction systems besides of the case of very viscous liquids, and the equilibrium state reaches in a few minutes through conventional Craig's discontinuous counter-current extraction apparatus like shaking[1]. Thus, it is reasonable to consider the first factor (formation rate) causes main difference in extraction rate.

Generally, the formation of extractable metal complex in the ion association extraction system is very rapid but those in the chelate extraction system is relatively slow and the distribution ratio increases with the shaking period (except some case of decreasing by such as hydrolysis[2]).

It was already pointed out[3][4] that the extraction rate changes by varying the acidity and/or the concentration of solvent for a system in which the formation rate of chelate controls the extraction rate. When the extraction systems are conditioned, for which such factors do not affect to the extraction rate seriously, it may be possible to study the different characteristics of extraction rate of each elements comparatively. It is also of interest to study whether the rate controlling factor is the concentration of solvent and/or acidity or final distribution ratio in a particular extraction system. Lanthanide elements and actinide elements in

trivalent state are specially interested to author for these problems because the different ionic radius (except some possible influence due to the different degree of availability of f orbital electrons in hybridization) seems to be main factor to result in different behavior. On the other hand extraction temperature should affect not only to the distribution ratio but also to the distribution rate because of it's influence to the formation of extractable chemical species.

Any quantitative study of this factor is very difficult and requires precise thermodynamical treatment but some qualitative study may be relatively simple. The elements in lanthanide and actinide series in trivalent state show many similarities each other in chemical behavior but they sometimes show abrupt varition of the characteristics between the lighter and heavier groups in solvent extraction as are shown in the study of their non-monotonic ording[5][6][7]. For present study Di-(2-ethyl hexyl) ortho phosphoric acid (HDEHP) is chosen as an organic solvent for the chelate form extraction and tri-n-octyl phosphine oxide(TOPO), tributyl phosphine oxide (TBPO) and tri-n-butyl phosphate (TBP) are chosen for the ion association form extraction.

EXPERIMENTS

Source of materials : HDEHP, supplied by Wako, Japan, was further purified according to the same method as D. F. Peppard et al described[8]. The purity was checked by measuring distribution ratio(Kd)*and acidity dependencies of Pm^{147} and Eu ^{152,154} Bi^{207} was obtained from Radio Chemical Center, England. Sc^{76} Pr^{142}, Tb^{160}, Lu^{177}, La^{140} and Th^{233} were prepared by neutron irradiation at TRIGA reactor ($\phi\sim10^{12}$). The target materials were >99.9% purity grade and were received from Research Chemical Inc. U. S. A., except Sc. and Th target. Spectrographically standard grade thorium nitrate and scandium oxide were received from Johnson Matthey Co., England. Other chemicals or radioactive tracers used are the same as in previous work[9]

Extraction apparatus: Water jacketed double reaction cell was used for controlling the reaction temperature. This cell was mounted on a motor driven shaking machine and the shaking rate was controlled by means of a transformer. The shaking speed was always adjusted to 60 ± 3 cycle per minutes. The temperature was controlled by continuous water flowing through the cell jacket from the ultra-thermostat. The shaking period was 20 minutes for HDEHP system and 5 minutes for other solvent system for the study of the effect of temperature to the distribution ratio.

Extraction : An aliquot amount of pre-equilibrated organic phase and aqueous phase was taken in the cell. The tracer was added just prior to start actual extraction operation. The temperature in the cell was pre-adjusted by flowing the water for two minutes through the jacket before starting actual shaking.

After shaking for pre-determined period, it was transfered into centrifuge cell immediately and the both phases were separated by double centrifugal operation. Every possible caution was taken to avoid fluctuation in the condition throughout the experiments such as temperature, shaking time and centrifugal operation.

Radioassay: Gamma counting was carried out with NaI(Tl) well type scintillator. RCL 256 multichannel analyzer with $3''\times3''$ NaI(Tl) scintillator or solid detector (C-4-25-0.2, supplied by RCA Victor, Canada) was used for γ or α spectrum analysis respectively.

RESULTS AND DISCUSSION

The results with Pr, Pm, Eu, Tb, Tm, Lu, Am, Cm, Bi and Th for the system of HDEHP-Toluene-HCl for 3 and 20 minutes shaking period are shown in Table 1. The temperature was set to 30°C except three additional data for Pm, Tm and Am at 2°C. Table 2 shows the measured distribution ratios of Pm, Eu, Tb, Tm, Lu and Am for various shaking periods for the same extraction systems as Table 1. These results show the extraction rates of lighter lanthanides ($Z<63$) are similar each other and are much greater than that of heavier lanthanides and the equilibrium state of distribution of lighter lanthanides can be achieved in less than 5 minutes for the used conditions. On the other hand, the distribution ratios steadily increase up to 20 or 30 minutes for heavier groups

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*The distribution ratio was defined as the ratio of counted activity of organic phase to that of aqueous phase under equal volume base.

TABLE 1. Kd vs. EXTRACTION TIME IN ADEHP-HCI SYSTEM(1)

element	HDEHP (%)(V/V)	HCI (N)	Temp. (°C)	Kd 3m	Kd 20m
Pr	35	0.1	30	2.142	2.103
Pm	15	0.1	30	1.110	1.090
Pm	15	0.1	2±0.2	0.982	0.980
Eu	15	0.2	30	0.881	0.894
Tb	16	0.3	30	1.449	2.056
Tm	10	0.6	30	0.615	2.781
Tm	10	0.6	2±0.2	0.080	0.527
Lu	7	0.8	30	0.189	1.553
Am	15	0.05	30	1.625	1.611
Am	15	0.05	2±0.1	1.489	1.484
Cm	10	0.04	30	1.183	1.185
Bi	10	0.1	30	2.604	2.612
Th	3	0.8	30	5.042	9.155

*The each value shown here is arithmetical mean value of three separate results.

condition but mainly from the original character of elements. The results for Am and Cm are similar to that of lighter lanthanides. The Kd values at lower temperature are smaller than that of higher temperature for same element (the reverse tendency was observed by C. A. Blake et al[11] for U) but the variation trends of extraction rate are the same for the both

TABLE 3. Kd vs. EXTRATION TIME IN HDEHP-HNO₃ SYSTEM

Element	HDEHP (%) (V/V)	HNO₃ (N)	Temp (°C)	Kd 3m	Kd 20m
Pr	50	0.2	30	3.014	3.050
Eu	30	0.4	30	0.868	0.901
Tb	15	0.3	30	0.916	1.976
Tm	10	0.6	30	2.005	2.508
Lu	10	0.7	30	3.491	9.527
Am	15	0.05	30	2.005	1.967
Cm	30	0.1	27	1.948	1.950

TABLE 2. Kd vs. EXTRACTION IN HDEHP-HCI SYSTEM(2)

Element	HDEHP (V/V) (%)	HCI (N)	Temp (°C)	Kd 3m	Kd 5m	Kd 10m	Kd 20m9	Kd 30m
Pm	12	0.1	30	0.729	0.780	0.784	0.782	
Eu	15	0.3	30	0.268	0.273	0.270	0.272	0.271
Tb	15	0.3	30	1.125	1.370	1.721	1.866	1.868
Tm	10	0.5	30	0.565	0.897	1.858	2.361	2.450
Lu	7	0.8	30	0.146	0.297	1.169	1.560	
Lu	7	0.8	4.5±0.2	0.053	—	0.147	0.211	
Am	15	0.05	30	1.612	1.640	1.613	1.622	1.630
Am	15	0.05	2±0.2	1.462	1.490	1.481	1.472	1.480

and, although the quantitative verification is not sufficient, the extraction rates seems to be getting smaller with the increasing atomic number. To make the magnitude of equilibrated distribution ratio similar each other the concentration of solvent and acidity are adjusted case by case, and, in general, the acidity should be higher for the case of heavier lanthaides than the case of lighter part. As Rubin[10] pointed out this may cause the variation of extraction rate. But, examining the results for Pm, Eu and Tb in Table 1 and for Eu and Tb in Table 2, it is obvious that the resulted differences in the extraction rates are not derived only from the sole effect of extraction

cases. Bi shows similar trend to the lighter lanthanides and tetravalent Th shows similar trend to the heavier part of lanthanides. Table 3 shows the results for Pr, Eu, Tb, Tm, Lu, Am and Cm in HDEHP-toluene-HNO₃ system. These are essentially the same as that of Table 1 and 2. Examining these results it is understood, especially for the heavier part, that the extraction rate have some relation with the ionic radius of each element under same condition. Am and Cm correspond to the first part of lanthanide series in this aspect.

The distribution of Am for the system of 2% (w/v) TOPO-toluene-0.01 N HNO₃ -0.24 M NH₄NO₃ at

TABLE IV. Kd vs. EXTRACTION TIME IN TOPO-HNO₃-NH₄NO₃ SYSTEM

Element	TOPO (%) (w/V)	(NO⁻₃)	Temp (°C)	Kd					
				3m	5m	10m	20m	30m	60m
Am	2	0.01 NHNO₃ 0.24 MNH₄NO₃	1.5±0.2	3.871	5.812	5.801	5.786	5.841	5.805
Am	2	"	20	0.704	0.998	1.021	0.988	1.002	1.010
Am	2	"	30	0.401	0.404	0.397	0.398	0.406	0.404

three different temperatures are shown in Table 4
The distribution reached in equilibrium in 5 minutes
at every temperature studied. This means that the
distribution rate of Am in the HDEHP extraction sys-
tem does not much differ from that in the ion associat-
ion extraction system.

The possible change of the extraction rate due
to the concentration of solvent or acidity was checked.
The time dependency of Kd/Kde of Tm at various
concentration of HDEHP and acidity are measured
and the results for the four systems are shown in Fig. 1
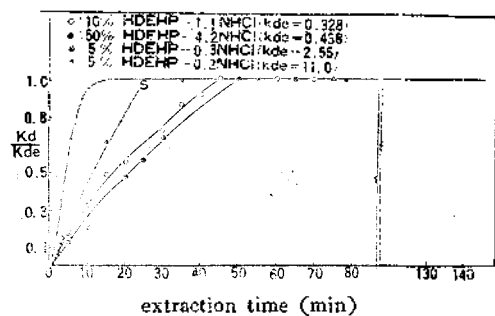
Fig. 1. Kd/Kde vs. extraction time for Tm in HDEHP-
HCl system.

Fig. 2. Kd/Kde vs. extraction time for Sc in HDEHP-
HCl system.
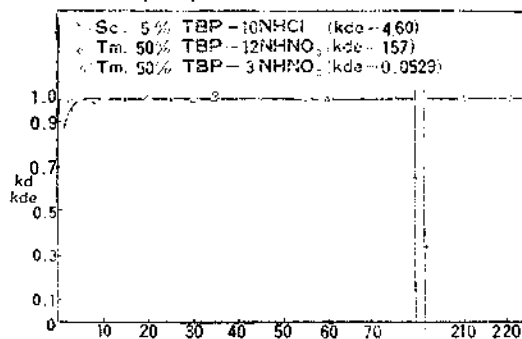
Fig. 3. Kd/Kde vs. extraction time in TBP-HCl or
HNO₃ system.

Here, Kde designates the Kd value at equilibrium
state. Fig. 2 shows the similar results with Sc in the
two systems.

These results show us the extraction rate or same
element in same solvent system is decided by the final
Kd value and greater the Kde value faster reaching final
equilibrium state. Fig. 3 shows the time dependencies
of Tm and Sc for TBP-toluene-HCl or HNO₃ system.
As is expected the rates are too great to differentiate
at higher or lower Kde value.

Fig. 4 shows the variation of Kd values with the
extraction temperature for Pm, Tm, Lu, Am and
Cm. These five straight lines show linear relation
between the Kd and temperature although the slopes

are different each other. It is interesting to note that
the slopes of three lines for Pm, Am and Cm are
nearly the same and smaller than that for Tm and Lu.
The slope of the line for Lu is larger than that for
Tm. Fig. 5 shows the relation between Kd and temp-
erature for Pr, Pm, Tm, Lu and Am.

General decreasing trends of the Kd value with
increasing temperature are observed. The common tre-
nds of changing to smaller slope suddenly at arround
15°C are also observed.

In Fig. 6 the variations of Kd vs temperature for
La Pr, Sm, Tm, Lu and Am in the system of
TBPO-HNO₃-NH₄NO₃ are plotted. Here, again, the
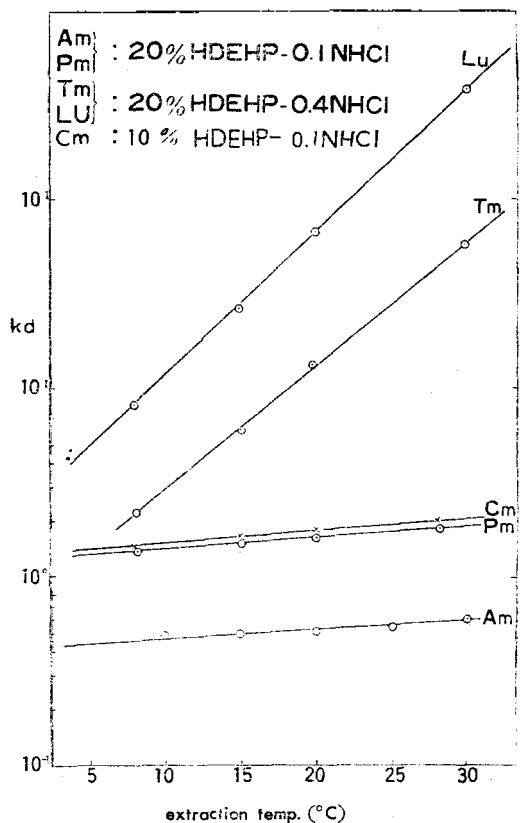value abrubtly at arround 15°C which is contrary to

Fig. 4
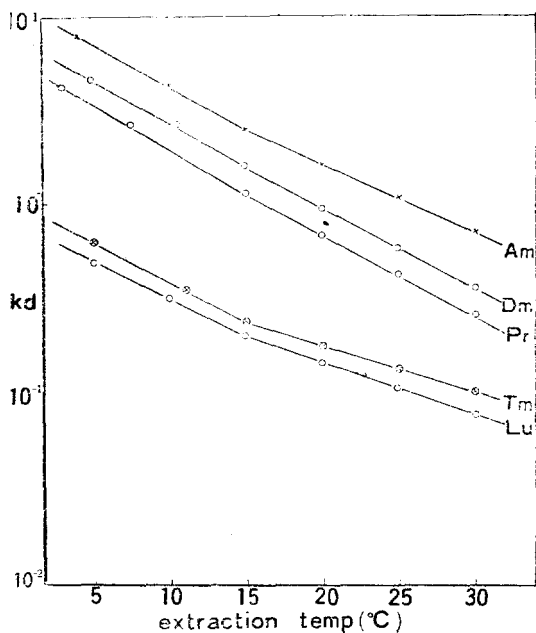

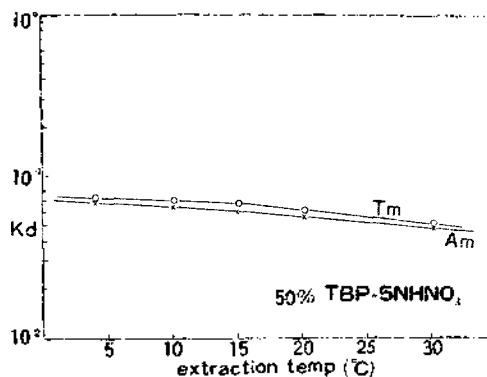FIUGRE. 5. 5Kd vs. Temp. for Pr, Pm, Tm, Lu & Am in TOPO-HNO₃-NH₄NO₃-system.

Fig.. 6. logKd vs. Temp for La, Pr, Sm, Tm, Lu & Am in TBPO-HN₃ NH₄NO₃ system.

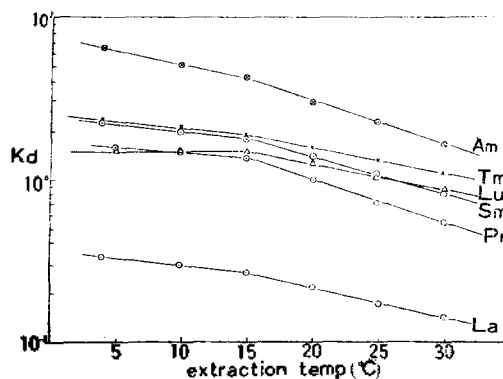
Fig.. 7. log Kd vs. Temp. for Am & Tm

the case of TOPO.

The observed relation of Kd vs temperature for Kd values decreases with increasing temperature linearly but the decreasing rate is changed to a larger Tm and Am in the extraction system of TBP-HNO₃ are shown in Fig. 7. The general trend is the same as the case of TBPO but the decreasing rate is smaller than the case of TBPO.

Through in these experiments no marked difference in the variation of Kd vs extraction temperature between the lighter and heavier lanthanous for ion association extraction system is observed, but the difference was quite obvious for HDEHP system.

Judging with the slopes of the lines in Fig. 4 and numerical calculation, it is obvious that the speration factor between adjacent element in the sense of atomic number in heavy lanthanide series varies appreciably with extraction temperature and the separation factor

will be getting smaller with decreasing temperature. On the other hand the separation factor for the lighter group of lanthanous remain constant throughout the experiments and it's value is calculated as ~2.5 which corresponds to the reported value. [8] As a consequence it may be postulated that the log Kd vs Z curves at various temperature will show similar variation as the case of neutral phosphorus compounds and it will show one straight line only at some arround room temperature. If these trends continue monotonically to the higher temperature the mutual separation of individual elements in heavy group of lanthanous will be easier at higher extraction temperature than at room temperature for the HDEHP system. There is observed no difference between the behavior of Am and Cm and are similar to that of Pm.

These results can be summerized as follows:

i) The distribution rates of the lighter part and the heavier part of lanthanides are different appreciably in the HDEHP extraction system. For lighter part the rates are similar each other but the rates seems to be getting smaller by increasing atomic number in heavier elements.

ii) The distribution rates of trivalent Am and Cm are similar with that of the lighter elements of lanthanides.

iii) The extraction temperature does not alter the said characteristics of the extraction rates.

iv) The distribution rate of an element with same chelate extraction system is mainely decided by the magnitude of final distribution ratio rather than the individual factor of solvent concentration or acidity.

v) The extraction rates of the lighter elements of lanthanides and trivalent Am or Cm in the HDEHP-HCl or -HNO$_3$ system are not differ appreciably from that of ion association extraction system.

vi) The distribution ratios of trivalent lanthanides and actinides increase with increasing extraction temperature for the HDEHP extractio system. The increasing rate of distribution ratio is getting larger with increasing atomic number for heavier lanthanides. Am and Cm are nearly same as the lighter elements of lanthanides in the variation rate.

vii) For ionic extraction system studied the distribution ratio shows decreasing trends with increasing temperature and no marked difference was observed in said trends between each element.

viii) At arround 15°C there appears some sudden change of decreasing rate of distribution ratio for ion association systems studied. For TOPO system it is changed to smaller value and contrarily, it is changed to larger value for TBPO system. For TBP extraction system it is essentially identical to the case of TBPO but the decreasing rate itself is smaller than the case of TBPO.

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4f 및 5f 系列 元素의 溶媒抽出에 있어서 分配速度를 測定해 본 結果 4f 系列의 前半部와 後半部 間에 明白한 差異를 볼 수 있었다. 三價의 Am 및 Cm은 4f 系列의 前半部와 類似함을 알았다. 또한 分配率과 抽出溫度와 의 關係를 檢討해 본 結果 抽出系에 따라 獨特한 增加 또는 減少傾向이 나타났으며 또한 Chelate 抽出系에 있 어서는 原子番號 依存性이 있음을 알았다.