

Extraction of Am(III) and Eu(III) with dialkyldi (or mono) thiophosphinic (or phosphoric) acids

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Extraction of Am(III) and Ln(III) from NaClO₄ medium with di(2-ethylhexyl)dithiophosphoric acid (DEHDTP), di(2-ethylhexyl)monothiophosphoric acid (DEHMTP), di(2-ethylhexyl)monothiophosphinic acid (DEHMTPI), dihexyldithiophosphinic acid (DHXDTP), diheptyldithiophosphinic acid (DHPDTPI), dioctyldithiophosphinic acids (DODTPI), dinonyldithiophosphinic acid (DNDTPI), di(1-methylheptyl)dithiophosphinic acid (DMHDTPI) and di(2-ethylhexyl)dithiophosphinic acid (DEHDTP) in xylene has been investigated. The order of the extraction selectivity for Am(III) is DEHDTP > DEHMTPI > DEHMTP, DHPDTPI > DODTPI > DHXDTP > DNDTPI, DMHDTPI > DEHDTP > DODTPI, for extractants with 2-ethylhexyl alkyl, straight chain alkyl, branch chain alkyl, respectively. Using 0.1 mol/l NaClO₄ solution as aqueous phase, the slope values of the log*D*–pH and log*D*–log*C* curves are not integers, and the slope values for Am(III) are slightly higher than those for Eu(III), for all extractants. The relationship between the slope value and extraction conditions can be described as: $\log S = \lg(C_{HA}/C_M^{S/4}) + b$. In the presence of macro Eu(ClO₄)₃, the formula, $\log SF_{Am/Ln} = B - 2\log(C_{HL} - D_{Ln}/(D_{Ln} + 1)C_{Eu})$, can well describe the relationship between separation factor and the extraction condition. A high separation factor ($SF_{Am/Eu} = 2500$) is obtained by solvent extraction with 0.5 mol/l DEHDTP in toluene from 1 mol/l NaNO₃ solution.

Introduction

The separation of lanthanides and actinides is necessary in the field of radioactive waste disposal and radioactive analysis, but the separation of Am(III) from Ln(III) is usually difficult because of their similar chemical properties. However, there is a minor discrepancy between them. Am(III) is softer acid than Ln(III), although they all are hard acid.¹ Therefore, those extractants containing so-called soft donor atoms (N or S) have a better selectivity for Am(III) over Ln(III). Many studies^{2–4} including our series works^{5–7} have verified this viewpoint.

Since MUSIKAS^{8–10} reported the synergistic system of DEHDTP and tributylphosphate (TBP) had a high separation factor ($SF_{Am/Eu} \approx 50$) in 1985, the extraction with compounds containing S atoms has been widely investigated. ZHU¹¹ examined the synergistic effect of TBP and DEHDTP on the separation of Am(III) from Ln(III), however, the separation factor obtained was less than 50. In 1996, ZHU² reported that they had obtained very high separation factors ($SF_{Am/Eu} \approx 5000$) using purified Cyanex 301, whose main constituent is di(2,2,4-trimethylpentyl) dithiophosphinic acid. JÄRVINEN¹² reported that separation factors of 1000 were achieved between Am(III) and Eu(III) by combining extraction with dicyclohexyldithiophosphinic acid and TBP. MODOLO³ found that there were no detectable extraction in nitric acid medium when three kinds of diaryldithiophosphinic acids (aryl=C₆H₅–, ClC₆H₄–, CH₃C₆H₄–) were used alone as extractants for Am(III) or Eu(III), but high separation factors ($SF_{Am/Eu} > 20$) with $D_{Am} > 1$ were achieved by means of the synergistic

effect of DCPDTPI and TBP. Three kinds of dialkyldithiophosphinic acids (alkyl=n-octyl, 1-methylheptyl, 2-ethylhexyl) were synthesized and very high separation factors ($SF_{Am/Eu} \approx 1 \cdot 10^4$) were obtained by TIAN.⁴

The results mentioned above show that high separation factor can be indeed achieved by extraction with dialkyldithiophosphinic acids (DALDTPI). But the effect of chemical structures of those extractants on separation capability was not studied systematically, hitherto. In the present work, the effects of chemical structure of 9 kinds of dialkyldi (or mono) thiophosphinic (or phosphoric) acids on separation capability were revealed.

Experimental

Reagents

Di(2-ethylhexyl)monothiophosphoric acid (DEHMTP), di(2-ethylhexyl)dithiophosphoric acid (DEHDTP) and di(2-ethylhexyl)monothiophosphinic acid (DEHMTPI) were synthesized by the Liaoning University (in China). The characteristics of those extractants are shown in Table 1. Dihexyldithiophosphinic acid (DHXDTP), diheptyldithiophosphinic acid (DHPDTPI), dioctyldithiophosphinic acid (DODTPI), dinonyldithiophosphinic acid (DNDTPI), di(1-methylheptyl) dithiophosphinic acid (DMHDTPI) and di(2-ethylhexyl) dithiophosphinic acid (DEHDTP) were synthesized according to the procedure reported by TIAN⁴ in our laboratory. The characteristics of those extractants are listed in Table 2. Major impurities and purity (%) were also checked by GC-MS spectrometry.

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Considering that the major impurities have no effect on the extraction, these extractants were not purified further, although the purity of DHXDTPi and DNDTPi are more than 99%. The nine kinds of extractants can be divided into three series based on their chemical structures. DEHMTPI, DEHMTP, DEHDTPI and DEHDTP comprise 2-ethylhexyl series, whose alkyls are 2-ethylhexyl. Straight chain alkyl series includes DHXDTPi, DHPDTPI, DODTPI and DNDTPi; and branch chain alkyl series includes DODTPI, DMHDTPI and DEHDTPI, which are isomeric compounds.

^{241}Am was obtained from Amershem Radiochemical Center GB and ^{147}Nd , ^{152}Eu , ^{170}Tm from Chinese Institute of Atomic Energy. NaClO_4 was recrystallized twice with deionized water before used. All other chemical reagents used were of analytical grade.

Procedure

Extraction of tracer amount radioactive Am(III) and Eu(III): The organic solutions were prepared by dissolving weighed quantities of extractants in xylene. The aqueous solution was 0.1 mol/l NaClO_4 , in which tracer amount of radiotracers ^{152}Eu and ^{241}Am was added. After pH adjustment of aqueous phase with NaOH and HClO_4 solution, equal volumes of the organic and aqueous phase were equilibrated in 25-ml vials. The vials were shaken in a thermostatic water bath ($25 \pm 1^\circ\text{C}$) for 30 minutes. After centrifugation and phase separation, the pH value of the equilibrated aqueous phase was measured with a $\Phi 72$ pH meter (Beckman Instruments, Inc.). The activities of ^{241}Am and ^{152}Eu were measured with a well-type HPGe gamma-detector (Canberra Co.). The distribution ratios, D , of Am(III) and Eu(III) were defined as the quotient of specific activities of organic phase and aqueous phase. The statistical errors of radioactivity measurements were less than 1% ($0.01 < D < 100$) or 5% ($D < 0.01$ or $D > 100$). The errors of the slope values were less than 3%.

Extraction of macro amount lanthanides: The aqueous solutions were prepared by dissolving weighed quantities of $\text{Eu}(\text{ClO}_4)_3$ in 1 mol/l NaClO_4 solution, in which tracer amount of radiotracers ^{147}Nd , ^{152}Eu , ^{170}Tm and ^{241}Am was added. The other extraction procedures were the same as that of extraction of tracer amount radiotracers.

Results and discussion

Extraction with the extractants of 2-ethylhexyl series

At constant concentration of extractant (0.1 mol/l in xylene) and constant ionic strength (0.1 mol/l NaClO_4), the extraction of tracer amount radiotracers Am(III) and Eu(III) with DEHMTP, DEHDTP, DEHMTPI and DEHDTPI was performed under different pH values of aqueous phase. The dependences of $\log D$ on pH values of equilibrated aqueous phase are shown in Figs 1 and 2 shows the relationship between $\log D$ and the concentration of extractants at constant pH value and ionic strength (0.1 mol/l NaClO_4) for equilibrated aqueous phase. The $\text{pH}_{1/2}$ are the pH value of aqueous phase when D is 1. The separation factor ($SF_{\text{Am/Eu}}$) is defined as $D_{\text{Am}}/D_{\text{Eu}}$ under the same extraction conditions. According to Fig. 1, the $\text{pH}_{1/2}$ values of aqueous phases for extraction of Am(III) and Eu(III) by DEHMTPI, DEHDTPI, DEHMTP, DEHDTP are 1.11, 1.35, 2.35, 2.41, and 1.04, 1.37, 2.20, 2.43, respectively. Corresponding $SF_{\text{Am/Eu}}$ are 0.96 (pH 0.86), 4.2 (pH 2.36), 0.68 (pH 2.87), 2.43 (pH 3.13), respectively. Based on $\text{pH}_{1/2}$ and $SF_{\text{Am/Eu}}$, the order of extraction powers is $\text{DEHMTPI} > \text{DEHDTPI} > \text{DEHMTP} > \text{DEHDTP}$, and extraction selectivity for Am(III) is $\text{DEHDTPI} > \text{DEHDTP} > \text{DEHMTPI} > \text{DEHMTP}$. Dithiophosphinic (or phosphoric) acids, whose two O atoms are substituted by S atoms, are softer than monophosphinic (or phosphoric) acids in which only one O atom is replaced. Furthermore, Am(III) is 'softer' hard-acid than Ln(III). So, the extraction powers of DEHDTPI and DEHDTP are weaker than DEHMTPI and DEHDMTP, respectively, and the $SF_{\text{Am/Eu}}$ of DEHDTPI and DEHDTP are higher than those of DEHMTPI and DEHDMTP, respectively. In phosphinic acid, P atom connects to two C atoms, whose capabilities of attracting electron are weaker than those of two O atoms in phosphoric acid. The density of electron cloud around S atoms in phosphinic acid is greater than that in phosphoric acid. So phosphinic acids are softer than phosphoric acids. For this reason, the extraction selectivities of DEHDTPI and DEHMTPI are better than those of DEHDTP and DEHMTP, respectively. The results show that the extraction selectivities of dithiophosphinic (or phosphoric) acids are better than those of monothiophosphinic (or phosphoric) acids, and the extraction selectivities of phosphinic acids are better than those of phosphoric acids. It implies that the dithiophosphinic acids may be the most promising extractants for separating Am(III) from Ln(III). This is not only an important conclusion of this paper, but also a basic idea of the present work.

Table 1. Characteristics of three kinds of extractants

Extractants	Purity, %	Density, g/ml	Diopter (n_D^{20})	Major impurity
DEHMTP	99	0.9770	1.4563	2-ethylhexyl alcohol
DEHDTPI	99	0.9802	1.4709	2-ethylhexyl alcohol
DEHDTPI	99			2-ethylhexyl alcohol

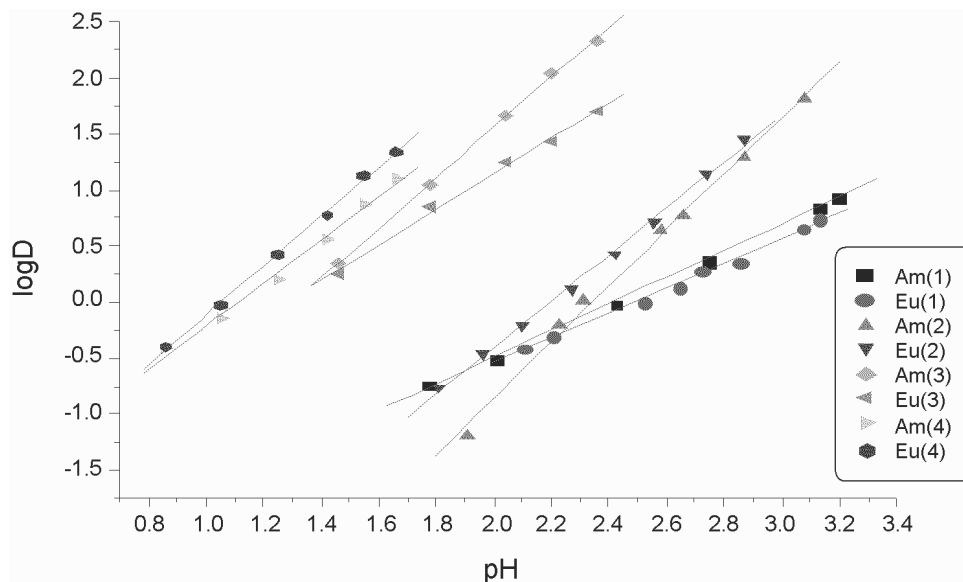


Fig. 1. Dependence of $\log D$ on pH (1) DEHDTPI, (2) DEHMTP, (3) DEHDTPI, (4) DEHMTPI, 0.1 mol/l extractants in xylene/tracer amount of ^{241}Am and ^{152}Eu in 0.1 mol/l NaClO_4

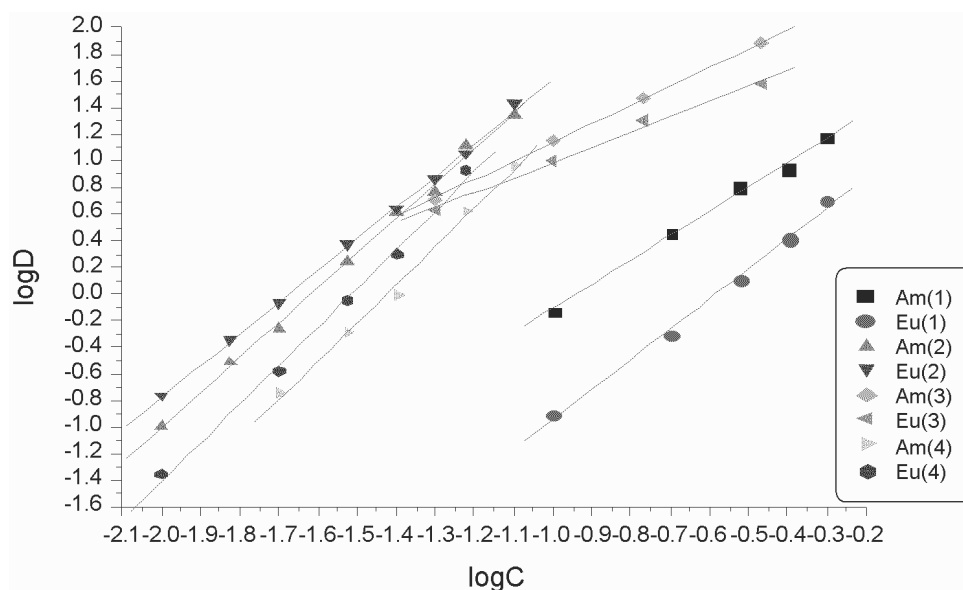


Fig. 2. Dependence of $\log D$ on $\log C$ (1) DEHDTPI (pH 2.24), (2) DEHMTP (pH 2.97), (3) DEHDTPI (pH 1.84), (4) DEHMTPI (pH 1.74); tracer amount of ^{241}Am and ^{152}Eu in 0.1 mol/l NaClO_4

Table 2. Characteristics of the six kinds of DALDTPIs

Extractants	Purity, %	Elemental composition and calculated values, %			Major impurity
		C (Cal.)	H (Cal.)	S (Cal.)	
DHXDTPI	98	51.75(51.14)	10.59(10.15)	23.69(24.06)	Hexane
DHPDTPI	99	57.32(57.14)	10.80(10.54)	21.89(21.77)	Heptane
DODTPI	99	60.21(59.63)	10.90(10.87)	19.97(19.88)	Octane
DNDTPI	95	63.56(61.71)	11.87(11.14)	17.02(18.29)	Nonane
DMPDTPI	99	59.88(59.63)	10.21(10.87)	19.38(19.88)	1-Methylheptane
DEHDTPI	99	60.03(59.63)	11.02(10.87)	19.17(19.88)	2-Ethylhexane

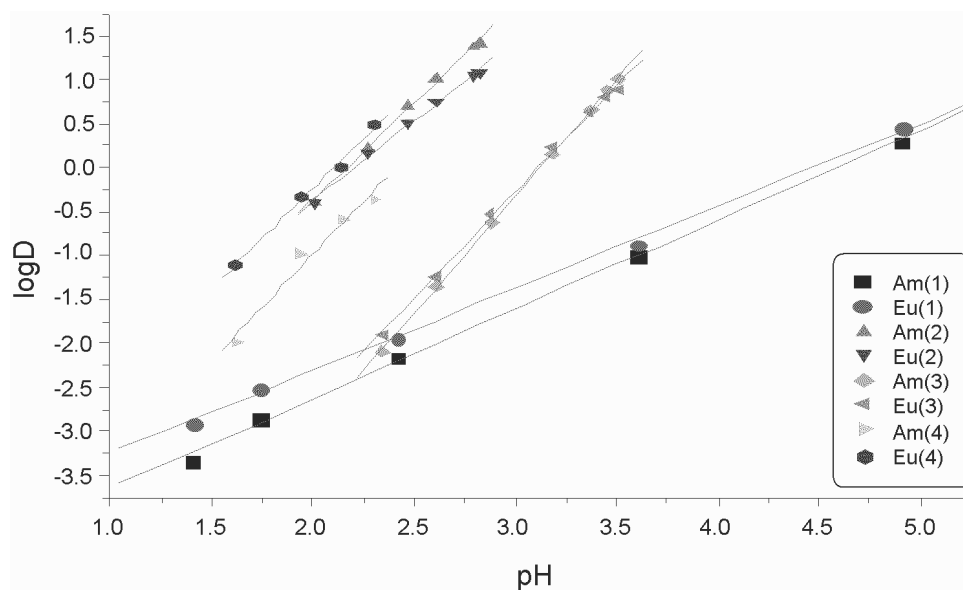


Fig. 3. Dependence of $\log D$ on pH (1) DHXDTPI, (2) DHPDTP, (3) DODTPI, (4) DNDTPI, 0.1 mol/l extractants in xylene/tracer amount of ^{241}Am and ^{152}Eu in 0.1 mol/l NaClO_4

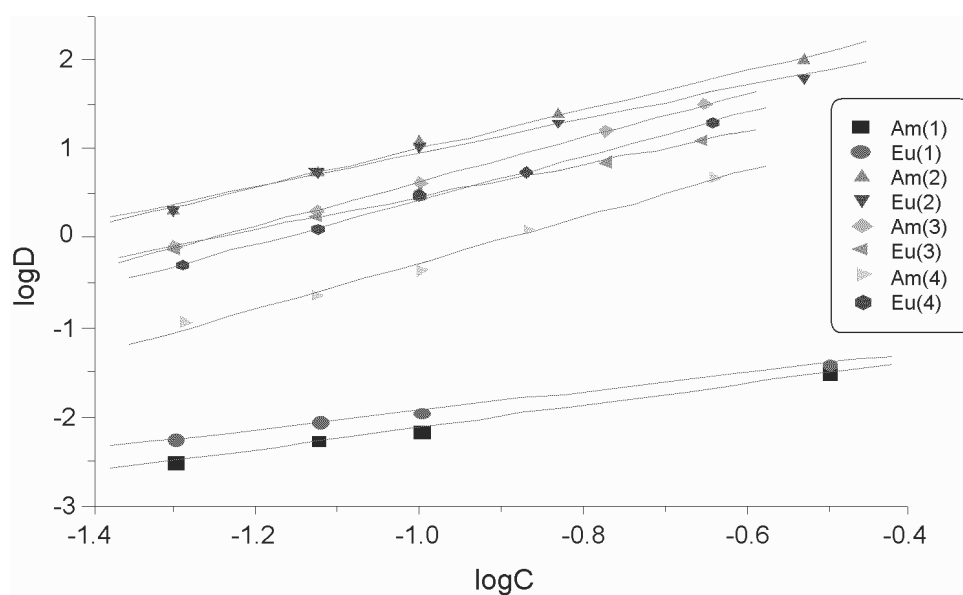


Fig. 4. Dependence of $\log D$ on $\log C$ (1) DHXDTPI (pH 2.41), (2) DHPDTPI (pH 2.58), (3) DODTPI (pH 3.33), (4) DNDTPI (pH 2.60); tracer amount of ^{241}Am and ^{152}Eu in 0.1 mol/l NaClO_4

Extraction with straight chain alkyl DALDTPI

As shown in Figs 3 and 4, the distribution ratios of Am(III) and Eu(III) when they are extracted by four straight chain alkyl DALDTPI increase with increasing of pH value and initial concentration of extractant. The $pH_{1/2}$ values of aqueous phases for extraction of Am(III) and Eu(III) by DHXDTPI, DHPDTPI, DODTPI, DNDTPI are 3.9, 2.10, 3.12, 2.43, and 3.6, 2.12, 3.12, 2.05, respectively. Corresponding $SF_{Am/Eu}$ are 0.71 (pH 4.90), 2.1 (pH 2.82), 1.4 (pH 3.51), 0.3 (pH 1.94), respectively. The order of the extraction powers of four straight chain alkyl extractants for Am(III) and Eu(III) is DHPDTPI \approx DNDTPI > DODTPI > DHXDTPI, and the order of extraction selectivities for Am(III) is DHPDTPI > DODTPI > DHXDTPI > DNDTPI. The extraction power is not simply rely on the number of carbon atoms in the alkyl. Maybe two or more properties of straight chain alkyl DALDTPI, such as molecular weight and aqueous dissolubility, and so on, affect the extraction power jointly. From the order of selectivities, DALDTPI with C-7 and C-8 alkyl have a better separation capability for Am(III) and Eu(III).

Extraction with branch chain alkyl DALDTPI

The results of the extraction of Am(III) and Eu(III) from 0.1 mol/l $NaClO_4$ using DODTPI, DMHDTPI and DEHDTPI in xylene are shown in Figs 5 and 6. The $pH_{1/2}$ values of aqueous phases for extraction of Am(III) and Eu(III) by DODTPI, DMHDTPI, DEHDTPI are 3.12, 3.15, 1.35, and 3.12, 3.45, 1.37, respectively. Corresponding $SF_{Am/Eu}$ are 1.4 (pH 3.51), 8.3 (pH 4.12), 4.2 (pH 2.36), respectively. According to their $pH_{1/2}$ and $SF_{Am/Eu}$, the order of extraction powers of Am(III) and Eu(III) is DEHDTPI > DODTPI \approx DMHDTPI, and the order of extraction selectivities for Am(III) is DMHDTPI > DEHDTPI > DODTPI. The extraction capability of DEHDTPI is the highest among three extracts. That can be attributed to the higher solubility of DEHDTPI in organic solvent. Because the capabilities of donating electron increase along the order of n-octyl < 2-ethylhexyl < 1-methylheptyl, the densities of electron cloud around S atoms become heavier in the same order, and the extractants become softer in order of DODTPI < DEHDTPI < DMHDTPI. Namely, DMHDTPI is the softest extractant in the noticed DALDTPIs, and its $SF_{Am/Eu}$ is the highest.

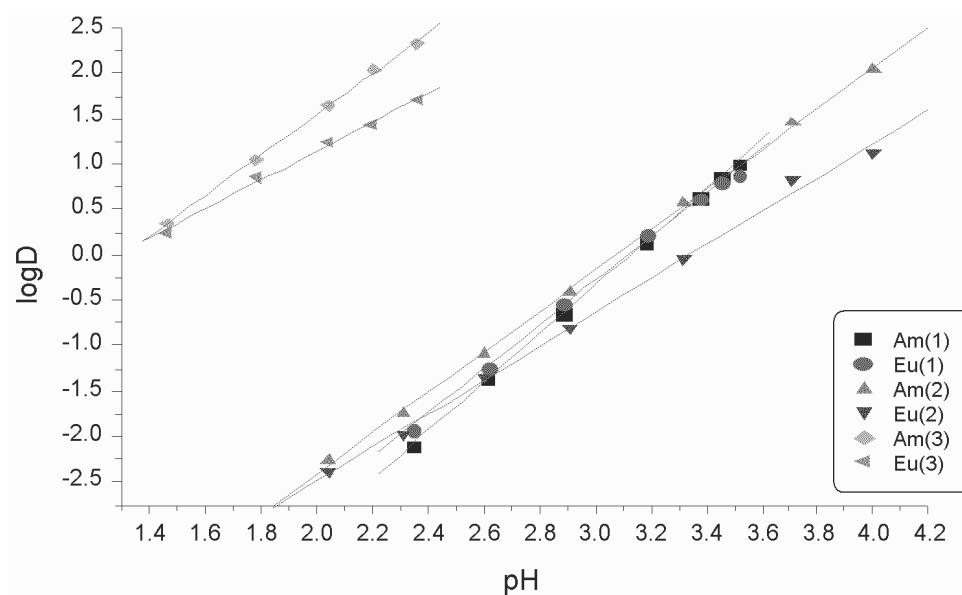


Fig. 5. Dependence of $\log D$ on pH (1) DODTPI, (2) DMHDTPI, (3) DEHDTPI; 0.1 mol/l extractants in xylene/tracer amount of ^{241}Am and ^{152}Eu in 0.1 mol/l $NaClO_4$

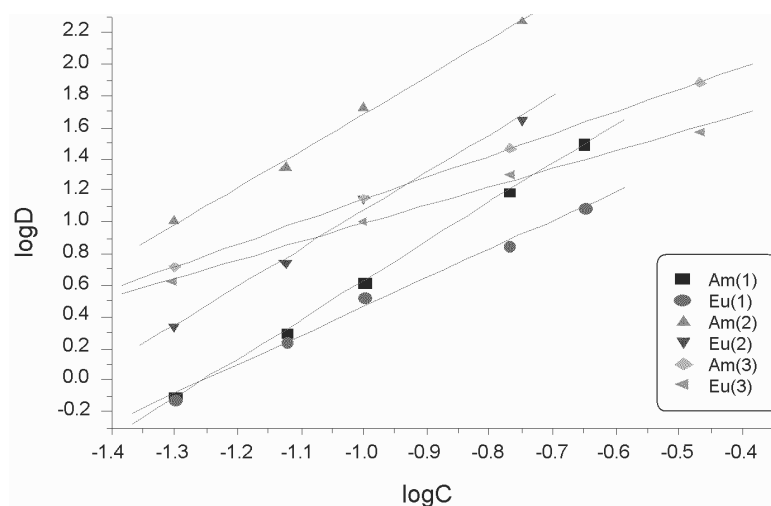


Fig. 6. Dependence of $\log D$ on $\log C$ (1) DODTPI (pH 3.33), (2) DMHDTPI (pH 3.62), (3) DEHDTPI (pH 1.84); tracer amount of ^{241}Am and ^{152}Eu in 0.1 mol/l NaClO_4

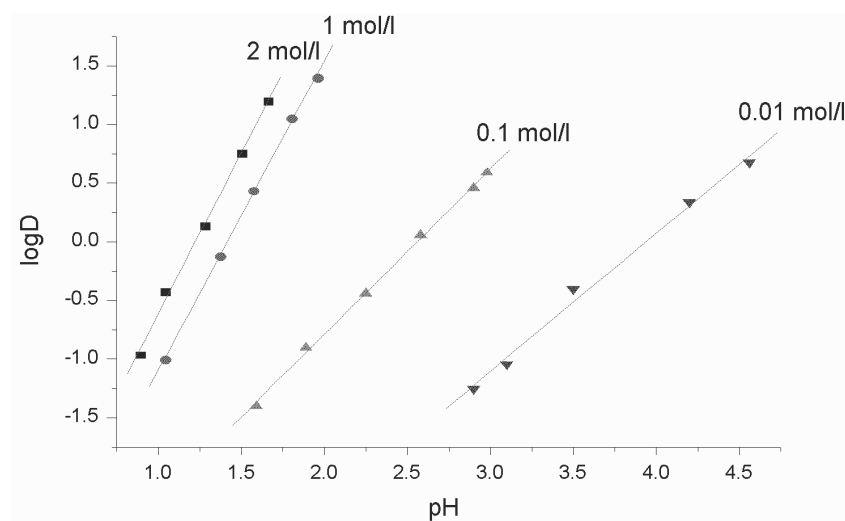


Fig. 7. Dependence of $\log D$ on pH. Various concentration of DEHDTP in xylene/tracer amount of ^{170}Tm in 0.1 mol/l NaClO_4

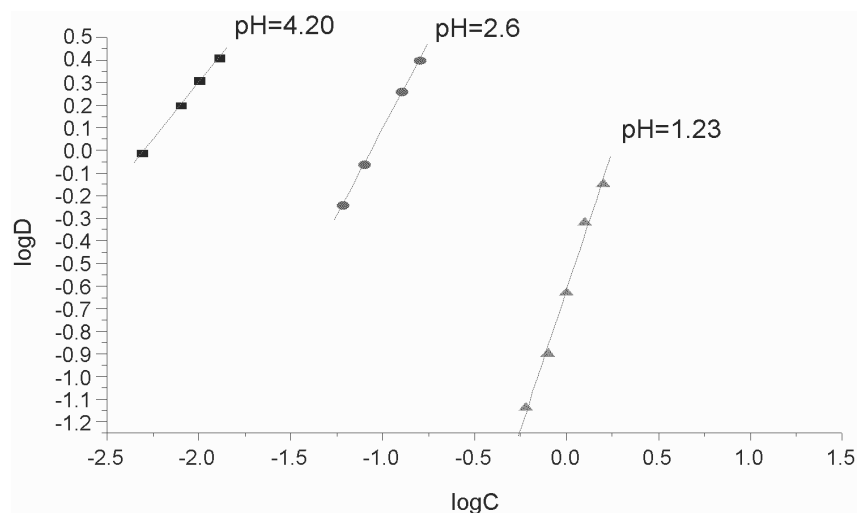


Fig. 8. Dependence of $\log D$ on $\log C$ tracer amount of ^{170}Tm in 0.1 mol/l NaClO_4

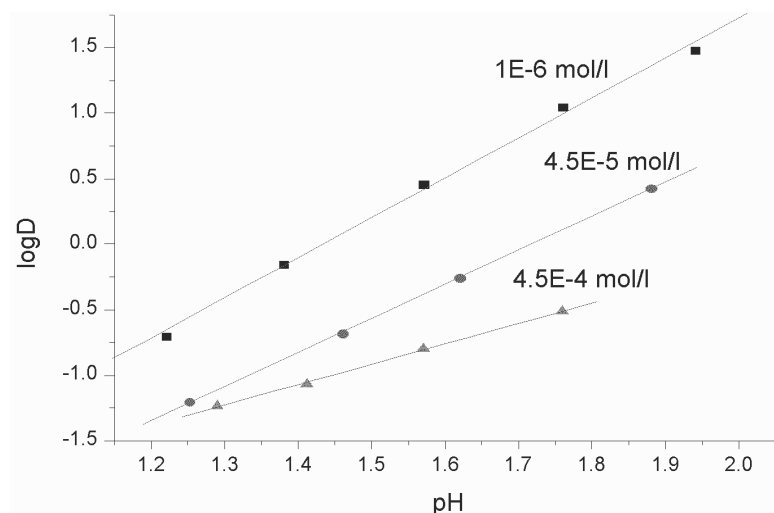


Fig. 9. Dependence of $\log D$ on pH value 0.1 mol/l DEHDTP in xylene/different concentrations of Tm(III) in 0.1 mol/l NaClO_4

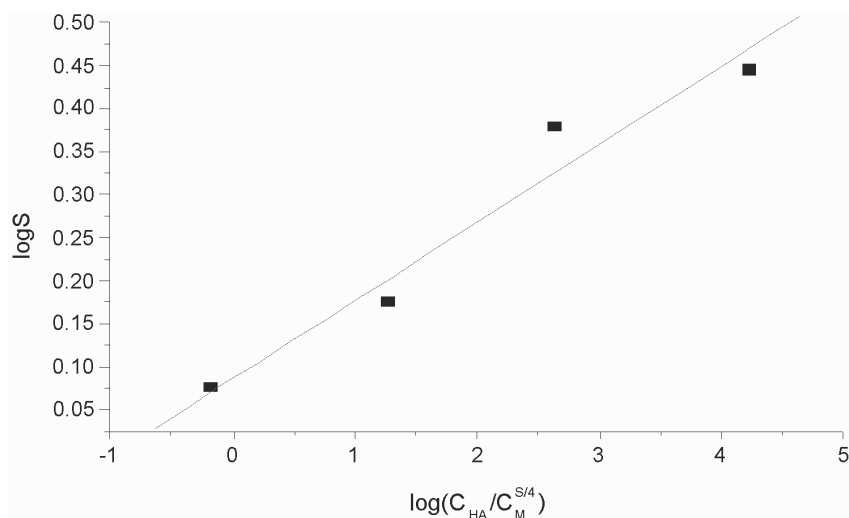


Fig. 10. Relationship between $\log S$ and $\log(C_{\text{HA}}/C_{\text{M}}^{S/4})$

The effect of extraction conditions on the slope values of $\log D$ –pH and $\log D$ – $\log C$

It can be seen from Figs 1–6 that, for nine kinds of extractants, the slope values of the straight lines for $\log D$ –pH and $\log D$ – $\log C$ are not integers, and the slope values for Am(III) are slightly higher than those for Eu(III). It is interesting that the slope values change with extraction conditions. When the concentration of extractants were 2 mol/l, 1 mol/l, 0.1 mol/l or 0.01 mol/l, a tracer amount of Tm(III) was extracted with DEHDTP. The slope values of $\log D$ –pH curves obtained are 2.79, 2.76, 1.5, 1.2, respectively (Fig. 7). When the concentrations of DEHDTP were within a small scope around 1 mol/l, 0.1 mol/l or 0.01 mol/l, respectively, a tracer amount of Tm(III) was also extracted. The slope

values of $\log D$ – $\log C$ curves are 2.0, 1.8, 0.8, respectively (Fig. 8). It can be seen from Figs 7 and 8 that the slope values of $\log D$ –pH and $\log D$ – $\log C$ curves increase with the concentration of DEHDTP. When the concentration of DEHDTP is around 1 mol/l, the plot of $\log D$ vs. pH becomes a straight line with the slope close to 3, and the slope value of $\log D$ – $\log C$ line is 2. Therefore, for DEHDTP in xylene, the extraction reaction of Tm(III) can be described by Eq. (1), where the subscripts “aq” and “org” refer to the aqueous and organic phases, respectively. From Eq. (1) the extraction constant K_{ex} is derived ($\log K_{\text{ex}} = -3.69$):



The slope value does not only change with extractant concentration, but also with Tm(III) concentration,

which is shown in Fig. 9. When the Tm(III) concentrations are 10^{-6} mol/l, $4.5 \cdot 10^{-5}$ mol/l and $4.5 \cdot 10^{-4}$ mol/l, the slopes of $\log D$ -pH curves are 2.8, 2.4 and 1.5, respectively. The phenomenon that slope value changes with extraction conditions implies that maybe more than one extraction complex is formed and the extraction mechanism is complicated. The slope value of $\log D$ -pH curves was close to 3, which reported by ZHU et al.,² may be due to a high concentration of purified Cyanex 301 (0.5 mol/l) being used.

According to the experimental results (Figs 7 and 9), the relationship between the slope value and extraction conditions can be described as an experiential formula (2), where S , C_M , C_{HA} refer to the slope value of $\log D$ -pH, the initial concentration of Tm(III), the initial concentration of extractant, respectively. As shown in Fig. 10, the plot of $\log S$ vs. $\log(C_{HA}/C_M^{S/4})$ is a straight line (slope = 0.012, intercept = 0.091).

$$\log S = \lg(C_{HA}/C_M^{S/4}) + b \quad (2)$$

The effect of macro Ln(III) on the extraction separation

In the presence of macro $\text{Eu}(\text{ClO}_4)_3$, the extraction of Am(III) and Eu(III) from 0.1 mol/l NaClO_4 solution by DEHDTP was performed. Figure 11 shows the relationship between $\log D$ and concentration of

$\text{Eu}(\text{ClO}_4)_3$. The results indicate that $SF_{\text{Am}/\text{Eu}}$ will increase with the concentration of $\text{Eu}(\text{ClO}_4)_3$. While $\text{Eu}(\text{ClO}_4)_3$ concentration becomes more than $3.2 \cdot 10^{-2}$ mol/l, the distribution ratios of both Am(III) and Eu(III) decrease rapidly, but the $SF_{\text{Am}/\text{Eu}}$ increases gradually and the maximum $SF_{\text{Am}/\text{Eu}}$ is 5.0. Therefore, a high $SF_{\text{Am}/\text{Eu}}$ can be obtained by increasing the concentration of lanthanide ions.

Under constant concentration of $\text{Eu}(\text{ClO}_4)_3$, the dependence of $\log D$ on pH value of aqueous phase is shown in Fig. 12. The slope value of $\log D$ -pH curve for Am(III) is 1, which is similar to extraction of tracer amount of Am(III), but the $\log D$ -pH curves of Eu(III), Tm(III) and Nd(III) are approximate to horizontal lines. This implies that the extraction mechanism of Am(III) is the same as that of extraction of tracer amount of Am(III), but the extraction mechanisms of Eu(III), Tm(III) and Nd(III) change remarkably in the presence of macro $\text{Eu}(\text{ClO}_4)_3$. When pH value is 4.46, $SF_{\text{Am}/\text{Nd}}$, $SF_{\text{Am}/\text{Eu}}$ and $SF_{\text{Am}/\text{Tm}}$ are 38.4, 27.8 and 38.2, respectively. Table 3 lists the results of extraction of Am(III), Nd(III), Eu(III) and Tm(III) with different concentrations of DEHDTP, which has been saponified and the saponification degree is 37.5%. It can be seen from Table 3 that the distribution ratios of all four ions decrease as concentration of DEHDTP reduces, but the separation factors increase inversely.

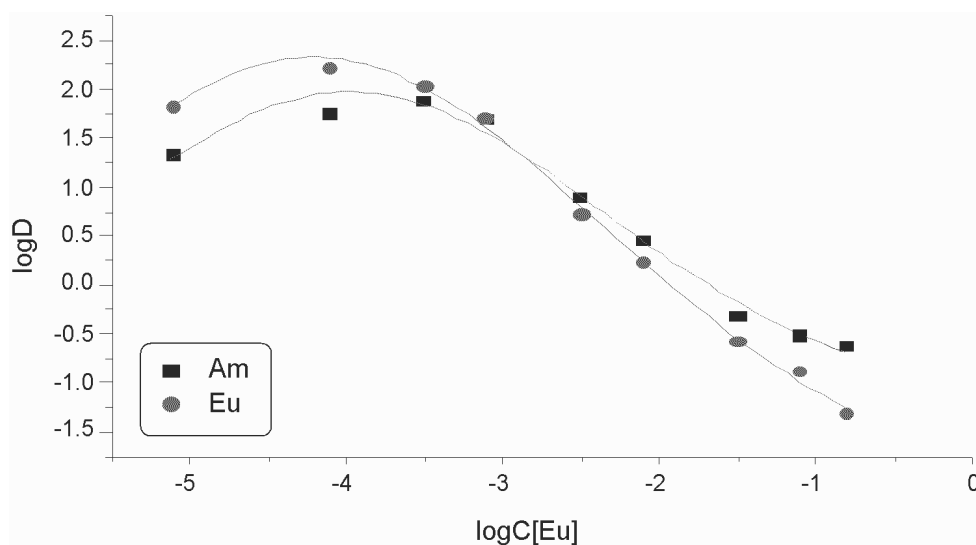


Fig. 11. Effect of concentration of $\text{Eu}(\text{ClO}_4)_3$ on $\log D$ 0.1 mol/l DEHDTP in xylene/1 mol/l NaClO_4 , pH 3.34

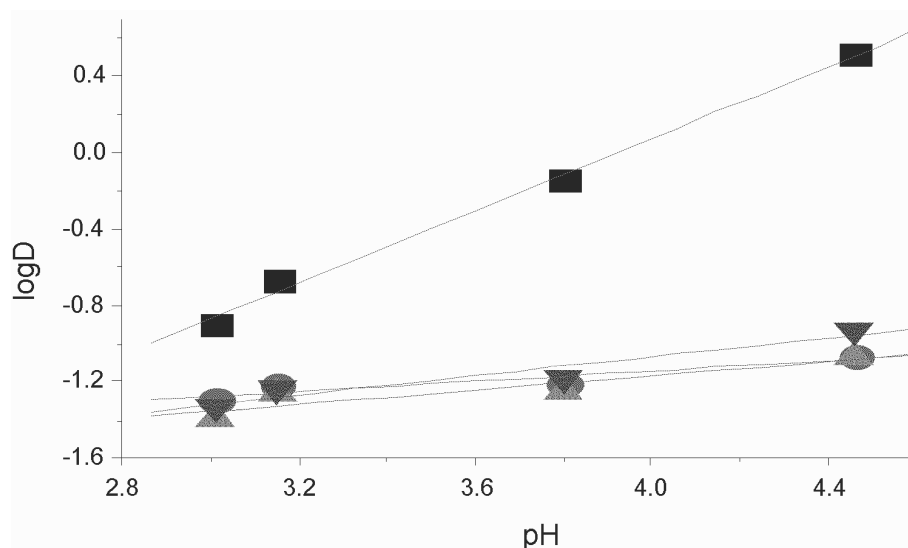


Fig. 12. Dependence of $\log D$ on pH value ■ Am, ▲ Nd, ▼ Eu, ● Tm.
DEHDTP = 0.1 mol/l, NaClO_4 = 1 mol/l, Eu(III) = 0.15 mol/l

Table 3. Effect of the concentration of DEHDTP on the distribution ratios and the separation factors in the presence of 0.15 mol/l $\text{Eu(ClO}_4)_3$

DEHDTP, $\text{mol}\cdot\text{l}^{-1}$	pH	D_{Am}	D_{Nd}	D_{Eu}	D_{Tm}	$FS_{\text{Am/Nd}}$	$FS_{\text{Am/Eu}}$	$FS_{\text{Am/Tm}}$
0.1	4.46	3.29	0.086	0.118	0.086	38.4	27.8	38.2
0.2	3.85	5.13	0.200	0.249	0.18	25.7	20.6	28.5
0.4	3.73	10.3	0.548	0.638	0.477	18.8	16.2	21.6
0.6	3.45	8.86	0.922	1.30	0.910	9.6	6.8	9.7
1.0	3.28	17.7	3.03	4.45	3.06	5.8	3.9	5.8

With a computer program designed by our group, an exponential formula (3) has been obtained, which can be expressed as:

$$\log SF_{\text{Am/Ln}} = B - 2\log(C_{\text{HL}} - D_{\text{Ln}}/(D_{\text{Ln}} + 1)C_{\text{Eu}}) \quad (3)$$

where C_{HL} , C_{Eu} , D_{Ln} , $SF_{\text{Am/Ln}}$ and B refer to the extractant concentration, concentration of $\text{Eu(ClO}_4)_3$, distribution ratio of lanthanide(III), separation factor between Am(III) and lanthanide(III) and a constant which relates to the extraction equilibrium constants, respectively. This formula can well describe the extraction results. It can be seen from this formula that the separation factor increases with the decreasing of concentration of extractant, or the increasing of concentration of macro $\text{Eu(ClO}_4)_3$ and distribution ratio of Ln(III). The pH value affects indirectly the separation factor by affecting D_{Ln} . Especially, when D_{Ln} is less than 1, it affects the separation factor remarkably (Fig. 11).

The effect of extraction medium on the $SF_{\text{Am/Eu}}$

In TIAN's paper,⁴ a much higher separation factors ($SF_{\text{Am/Eu}} \approx 1 \cdot 10^4$) than the $SF_{\text{Am/Eu}}$ obtained from Fig. 5,

was reported with three kinds of DALDTPI (alkyl = n-octyl, 1-methylheptyl, 2-ethylhexyl). Considering the extractants were synthesized in different laboratories, the micro amount of different impurities in extractants might affect the behaviors of extraction. The extraction experiments were conducted with DMHDTPI provided by TIAN under the same extraction conditions described as above. The result is shown in Fig. 13. It resembles to the plot of $\log D$ -pH shown in Fig. 5. This means that the difference between two $SF_{\text{Am/Eu}}$ is not due to the impurities in extractants. At the same extraction conditions as that reported by TIAN,⁴ the extraction with DEHDTP which was synthesized in our laboratory was carried out. The results is depicted in Fig. 14, and the highest $SF_{\text{Am/Eu}}$ is approximately 2500, which is still smaller than that of TIAN's, but it should be mentioned that the present separation factor is directly obtained from the extraction experiment while the TIAN's $SF_{\text{Am/Eu}}$ was calculated by $K_{\text{exAm}}/K_{\text{exEu}}$. The results indicate that the extraction conditions have a remarkable effect on the separation factor.

Using 0.1 mol/l NaClO_4 solution as aqueous phase, the separation factors for dithiophosphinic acids with different alkyls are obviously different, so the effect of

alkyl group on separation factor can be well compared, although the low separation factors are obtained. However, when using 1.0 mol/l NaNO_3 as aqueous phase, the $SF_{\text{Am/Eu}}$ values of DODTPI, DMHDTPI and DEHDTPI are high and close so that TIAN concluded the alkyl group structure of the extractants has no substantial effect on $SF_{\text{Am/Eu}}$. It is why the NaClO_4 medium is used in the present paper.

Conclusions

The extraction selectivity for Am(III) with dithiophosphinic (or phosphoric) acids is better than that with monothiophosphinic (or phosphoric) acids, whereas, the extraction selectivity for Am(III) with phosphinic acids is better than that of phosphoric acids. The branch chain alkyl DALDTPI have a higher extraction selectivity than straight chain alkyl DALDTPI.

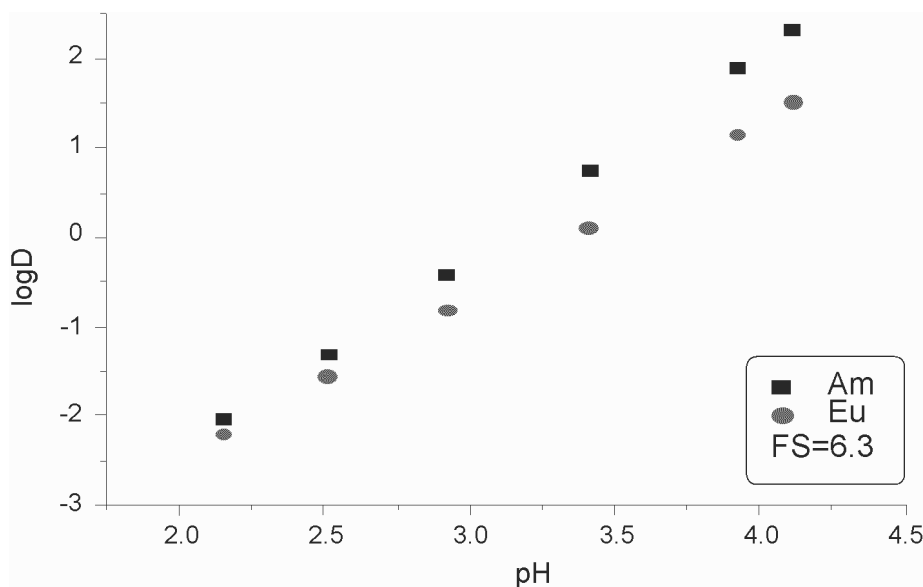


Fig. 13. Extraction with DMDTPI provided by TIAN, 0.1 mol/l DMDTPI in xylene/tracer amount of ^{241}Am and ^{152}Eu in 0.1 mol/l NaClO_4

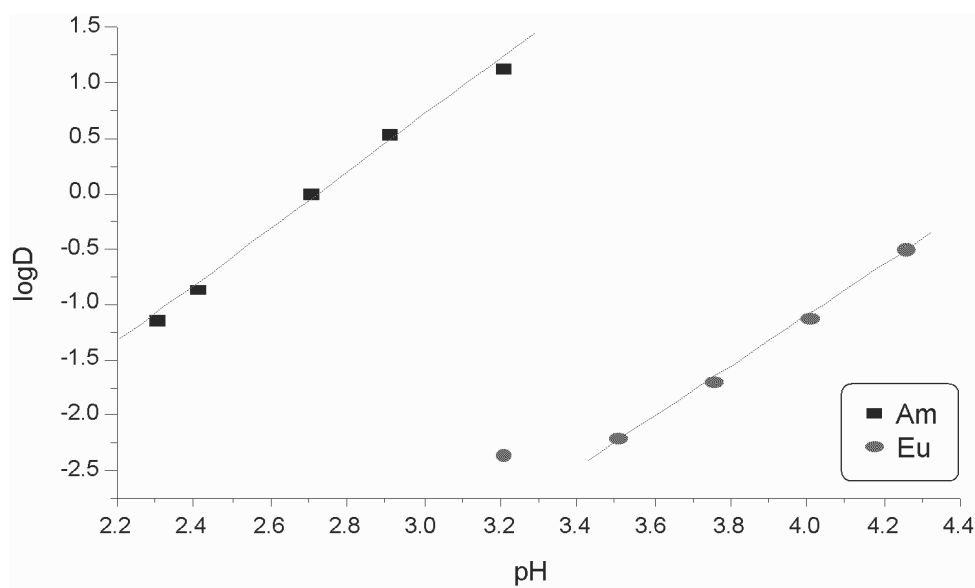


Fig. 14. Extraction with DEHDTPI synthesized in our laboratory; 0.5 mol/l DEHDTPI in toluene/tracer amount of ^{241}Am and ^{152}Eu in 1.0 mol/l NaNO_3

Using 0.1 mol/l NaClO_4 solution as aqueous phase, the slope values of $\log D$ -pH curves decrease with increasing of the concentration of extracted metal ions, or decreasing of the concentration of extractants. The relationship between the slope value and extraction conditions can be described as:

$$\log S = \text{alg}(C_{\text{HA}}/C_{\text{M}}^{S/4}) + b$$

In the presence of macro $\text{Eu}(\text{ClO}_4)_3$, the formula:

$$\log SF_{\text{Am/Ln}} = B - 2\log(C_{\text{HL}} - D_{\text{Ln}}/(D_{\text{Ln}} + 1)C_{\text{Eu}})$$

can well describe the relationship between separation factor and the extraction conditions. The separation factor increases with decreasing of the concentration of extractant, or increasing of the concentration of macro $\text{Eu}(\text{ClO}_4)_3$ and the distribution ratio of Ln(III). The pH value affects indirectly the separation factor by affecting D_{Ln} . Especially, when D_{Ln} is less than 1, it affects the separation factor remarkably.

The effect of extraction conditions on separation factor is very remarkable.

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