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Solvent extraction of lanthanides with triisoamylphosphate and di-(2-ethylhexyl)phosphoric acid from trichloroacetic acid and nitric acid solutions

Luu Minh Dai[a,*], Dang Vu Minh[a], Pham Van Hai[b]

[a]National Centre for Science and Technology of Vietnam, Institute of Materials Science, Nghia Do, Cau Giay, Hanoi, Viet Nam
[b]University of DaNang, DaNang, Viet Nam

Abstract

The study on solvent extraction of some rare earth elements with triisoamyl phosphate (TiAP) and a mixture of TiAP and di-(2-ethylhexyl)phosphoric acid (D2EHPA) from trichloroacetic acid and nitric acid solutions has been carried out. It was found that Y has been more effectively extracted with TiAP from the trichloroacetic acid solution than from the mono and dichloroacetic acid solutions. The influence of various factors such as acid, RE and salting-out agent concentrations on the distribution ratio has been studied. The synergistic extraction effects were observed for low trichloroacetic acid and high nitric acid concentrations. The influence of the TiAP–D2EHPA ratio and the total concentration of two extractants, as well as acid concentration on the synergistic extraction ratio has been investigated. RE extraction isotherms by TiAP and D2EHPA alone and by a mixture of these extractants in the above extraction systems were established. © 2000 Published by Elsevier Science S.A.

Keywords: Solvent extraction; Triisoamyl phosphate; Di-(2-ethylhexyl)phosphoric acid (D2EHPA); Rare earth elements; Extraction isotherms

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1. Introduction

Tri-*n*-butyl phosphate and di-(2-ethylhexyl)phosphoric acid are widely used as extractants for RE separations [1,2]. However, there are some studies relevant to the RE extraction with triisoamyl phosphate (TiAP) [3,4]. In this paper, we present results from study on RE extraction with TiAP and a mixture of TiAP and D2EHPA from trichloroacetic acid and nitric acid solutions.

2. Experimental

The RE solvent extraction with TiAP was carried out in a 50-ml separatory funnel. The phase volume ratio was 1:1. The duration of the solvent extraction was 5 min. After phase separation, the RE concentration in the aqueous phase was determined by DTPA titration with arsenazo III as an indicator. The acid concentration in the aqueous phase was determined by NaOH titration with methyl orange or phenolphthalein as an indicator. In the case of CH_3COOH before titration, the RE were separated by oxalate precipitation. Extractant concentration was given by volume percent.

The synergistic extraction ratio was given by [5]:

$$S_k = \lg \frac{D_{1,2}}{D_1 + D_2} \tag{1}$$

where $D_{1,2}$ is the distribution ratio in the system with two extractants, D_1 is the distribution ratio in the system with extractant 1 alone and D_2 is the distribution ratio in the system with extractant 2 alone.

The effect of synergistic extraction are positive if the value $S_K > 0$.

3. Results and discussion

3.1. Influence of equilibrium acid concentration on the yttrium distribution ratio in the Yx_3–Hx–50%TiAP–kerosene system ($x = CH_3COO^-$, $CHCl_2COO^-$, CCl_3COO^-)

In order to select a suitable aqueous solution for the RE extraction with TiAP, we studied the influence of the

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*Corresponding author. Tel.: +84-4-8363-082; fax: +84-4-8352-483.

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Table 1
Dependence of the Y distribution ratio on equilibrium acid concentration in the aqueous phase

$[H^+]_a$ (M)	Distribution ratio			
	CCl_3COOH	$CHCl_2COOH$	$CH_2ClCOOH$	CH_3COOH
0.004	–	0.104	–	–
0.005	1.380	–	–	–
0.010	0.763	0.032	–	–
0.025	0.308	–	–	–
0.037	–	0.009	0.003	–
0.043	0.176	–	–	0.002
0.065	0.083	–	–	–
0.074	–	0.006	–	–
0.103	–	–	0.002	–
0.125	–	0.004	–	–
0.137	0.027	–	–	–
0.180	0.020	–	–	0.001
0.200	–	0.002	0.002	–
0.305	–	–	0.001	–
0.430	0.007	–	–	–

equilibrium acid concentration on the yttrium distribution ratio. Results of the experiments are presented in Table 1.

From Table 1, it can be seen that the Y distribution ratio decreases in the row: $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$. Yttrium was very well extracted from the CCl_3COOH solution. It is due to the strong dissociation of CCl_3COOH facilitating the formation of complex between the cation, Y^{3+}, and the anion, CCl_3COO^-, which participates in the extraction process.

3.2. Influence of equilibrium acid concentration in the aqueous phase on the RE distribution ratio in the Lnx_3–Hx–50%TiAP–kerosene system

3.2.1. Trichloroacetic acid

The experiment was performed with an initial aqueous $Ln(CCl_3COO)_3$ concentration of 0.1 M. The results are illustrated in Fig. 1

From Fig. 1, it is found the RE distribution ratio is relatively high in an interval of low acid concentration from 0.005 to 0.030 M. At the higher acid concentration the RE distribution ratio decreases significantly. It is due to the competitive extraction of trichloroacetic acid into the organic phase.

3.2.2. Nitric acid

The experiment was performed with an initial aqueous $Ln(NO_3)_3$ concentration of 0.1 M. The results are illustrated in Fig. 2.

The results presented in Fig. 2 demonstrated that the distribution ratio reaches the maximum value in the interval of the equilibrium acid concentration in the aqueous phase from 2 to 4 M. After that an increase in acid concentration, a decrease of the RE distribution ratio results. It can be explained by competitive extraction of acid into the organic phase. However, a further increase of acid concentration in the aqueous phase facilitates the formation of the RE anion complex, which participates in the RE extraction process. The RE distribution ratio again increases at very high acid concentration.

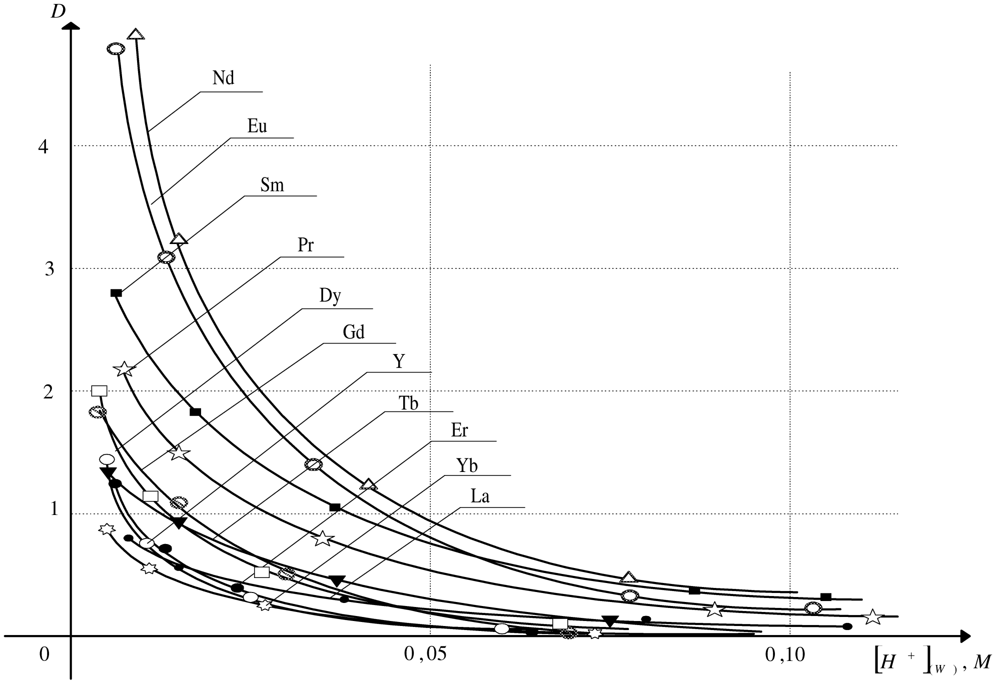

Fig. 1. Influence of $[H^+]_a$ on the distribution ratio of Nd, Eu, Sm, Pr, Dy, Gd, Y, Tb, Er, Yb and La in the 0.1 M $Ln(CCl_3COO)_3$–CCl_3COOH–50% TiAP–kerosene system.

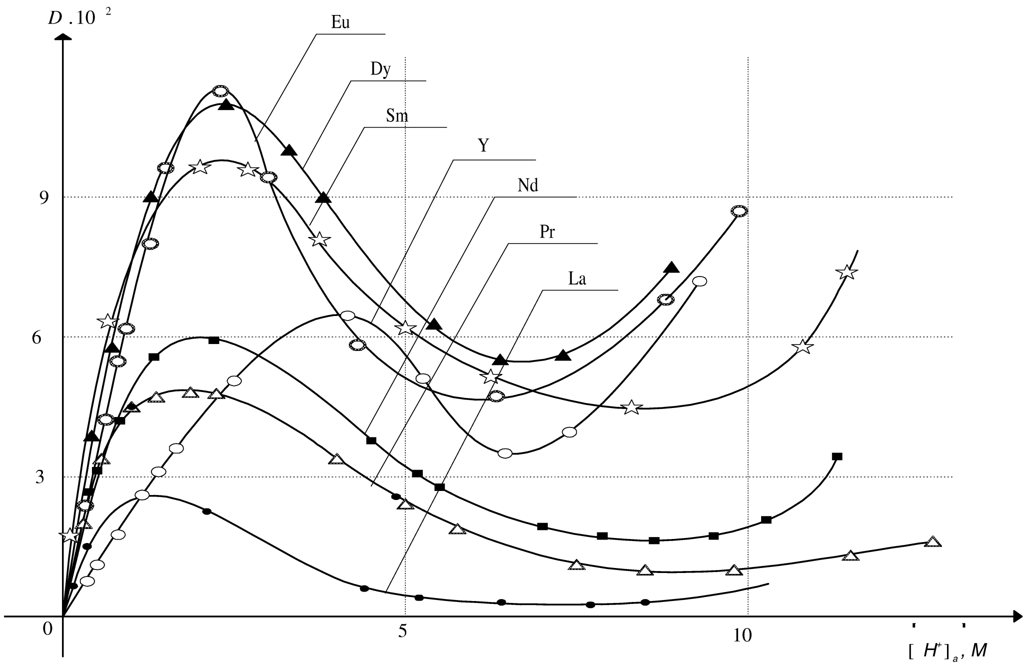

Fig. 2. Influence of $[H]_a$ on the distribution ratio of Eu, Dy, Sm, Y, Nd, Pr and La in the 0.1 M $Ln(NO_3)_3$–HNO_3–50% TiAP–kerosene system.

3.3. RE extraction isotherms in the Lnx_3–Hx–50% TiAP–kerosene system

The extraction isotherm is an important characteristic of an extraction system. The RE extraction isotherm in the $Ln(CCl_3COOH)_3$–CCl_3COOH–50% TiAP–kerosene and $Ln(NO_3)_3$–HNO_3–50% TiAP–kerosene systems are demonstrated in Fig. 3a and b.

The results presented in Fig. 3 show the following:

- In both the HNO_3 and CCl_3COOH solutions the RE with the higher distribution ratio have the higher extraction capacity.
- In the case of the CCl_3COOH solution, the RE extraction isotherms reach a maximum value at intervals of the equilibrium RE concentration in the aqueous phase of 0.2–0.3 M. A further increase of RE concentration in the aqueous phase results in a decrease of RE concentration in the organic phase. This is due to the competitive extraction of the acid into the organic phase.
- In the case of the HNO_3 solution, the RE extraction capacity is smaller than in the CCl_3COOH solution. The RE extraction isotherm achieves a maximum value when the equilibrium RE concentration in the aqueous phase is approximately 0.7 M.

3.4. Influence of salting-out agent concentration on the RE distribution ratio in the $Ln(CCl_3COO)_3$–CCl_3COOH–CCl_3COONa–50% TiAP–kerosene system

The experiment was performed under the following conditions: initial RE concentration was 0.1 M, initial acid concentration was 0.1 M and the salting-out agent concentration varied from 0 to 0.067 M. The results are presented in Fig. 4.

From Fig. 4, it can be seen that the RE distribution ratio increases when the salting-out agent concentration increases.

Compared to other system containing inorganic anions such as NO_3^-, Cl^- [6], in this case the influence of salting-out agent on the RE distribution ratio is higher.

3.5. The effect of synergistic extraction in nitric and trichloroacetic solutions

3.5.1. Nitric acid solution

The experiment was performed under the following conditions: initial concentration of $Dy(NO_3)_3$ was 0.1 M, concentration of HNO_3 was changed from 0.1 to 6 M. The results are presented in Table 2.

From Table 2, it can be seen that synergistic extraction occurred only when the HNO_3 concentration in the aqueous phase was higher than 1 M. In general, the effects of synergistic extraction are not strong in the HNO_3 solution.

3.5.2. Trichloroacetic solution

The experiment was performed under the following conditions: initial concentration of $Dy(CCl_3COO)_3$ was 0.1 M; concentration of CCl_3COOH varied from 0.5 to 3 M. The results are presented in Table 3.

From Table 3, the effects of synergistic extraction in a solution with the acid concentration lower than 1.5 M were found. An increase in the acid concentration resulted in a

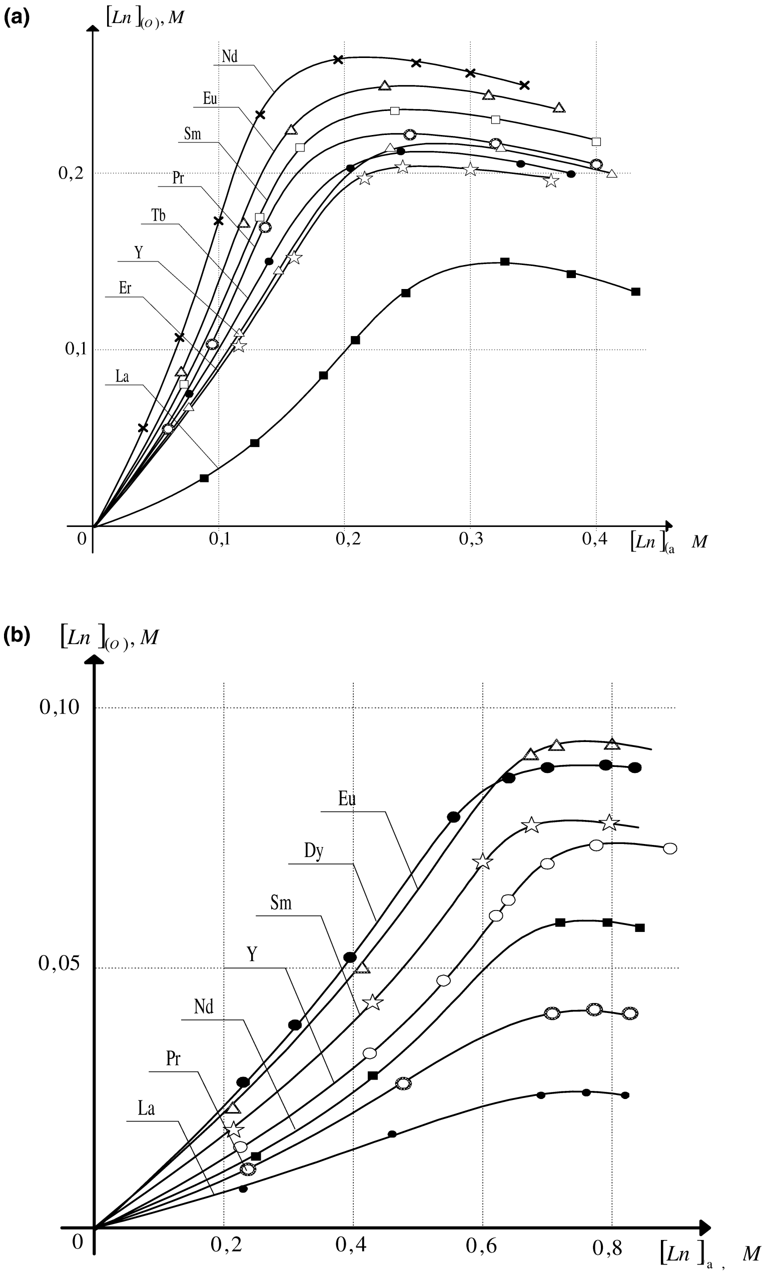

Fig. 3. (a) The extraction isotherm of Nd, Eu, Sm, Pr, Y, Tb, Er and La in the $Ln(CCl_3COO)_3$–0.5 M CCl_3COOH–50% TiAP–kerosene system. (b) The extraction isotherm of Eu, Dy, Sm, Y, Nd, Pr and La in the $Ln(NO_3)_3$–2 M HNO_3–50% TiAP–kerosene system.

decrease of D and S_k values. The Dy distribution ratio in the mixture of TiAP and D2EHPA was much higher compared to the systems with only one extractant.

3.6. Influence of some factors on synergistic extraction effect

3.6.1. Influence of TiAP–D2EHPA ratio

This experiment was performed under the following conditions: initial concentration of $Dy(NO_3)_3$ was 0.1 M, the total concentration of two extractants in kerosene was 50% and the TiAP–D2EHPA ratio varied from 3:1 to 1:3. The results are presented in Table 4.

As it can be seen from Table 4, the strongest effects of synergistic extraction occurred when the TiAP–D2EHPA ratio was 1:1. This ratio was then used for further experiments.

3.6.2. Influence of total concentration of extractants

The experiment was performed under the following conditions: $Dy(CCl_3COO)_3$ concentration was 0.1 M, CCl_3COOH concentration was 1 M and the total con-

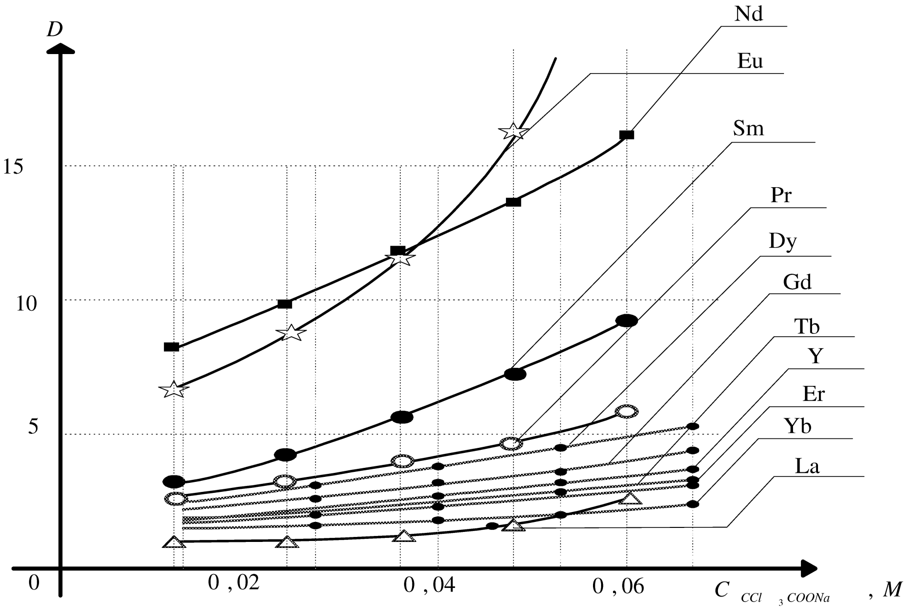

Fig. 4. Influence of CCl_3COONa concentration on the distribution ratio of Nd, Eu, Sm, Pr, Dy, Gd, Y, Tb, Er, Yb and La in the 0.1 M $Ln(CCl_3COO)_3$–0.1 M CCl_3COOH–CCl_3COONa–50% TiAP–kerosene system.

Table 2
Synergistic extraction in the $Dy(NO_3)_3$–HNO_3–TiAP+D2EHPA–kerosene system

C_H^+ (M)	d		D	S_k
	TiAP 25%	D2EHPA 255	TiAP 25%+D2EHPA 25%	
0.1	1.06×10^{-3}	6.59	4.87	−0.150
0.5	8.53×10^{-3}	2.66	2.61	−0.008
1.0	1.07×10^{-2}	1.25	1.29	0.013
2.0	5.14×10^{-2}	0.62	0.70	0.053
5.0	6.23×10^{-3}	0.24	0.31	0.110
6.0	4.07×10^{-3}	0.14	0.24	0.233

centration of the extractants varied but the TiAP–D2EHPA ratio remained 1:1. The results are presented in Table 5.

From Table 5 it can be seen that the higher the concentration of extractants, the stronger the effects of synergistic extraction are.

3.7.1. Influence of RE atomic number

The experiment was performed under the following conditions: RE concentration was 0.1 M and CCl_3COOH concentration was 1 M. The results are presented in Table 6. The data in Table 6 show that the effects of synergistic extraction increase with increasing RE atomic number.

3.8. Extraction isotherm of Dy in the $Dy(CCl_3COO)_3$–CCl_3COOH–TiAP, D2EHPA–kerosene system

The extraction isotherm is an important characteristic of the extraction process. In order to determine the extraction isotherm the experiment was performed under the follow-

Table 3
Synergistic extraction in the $Dy(CCl_3COO)_3$–CCl_3COOH–TiAP, D2EHPA–kerosene system

Extractant		C_H^+ (M)				
		0.5	1.0	1.5	2.0	3.0
TiAP 25%	D	0.17	1.8×10^{-3}	2.4×10^{-3}	1.9×10^{-3}	0.4×10^{-3}
D2EHPA 25%	D	27.0	4.07	3.15	1.68	1.44
TiAP 25%+D2EHPA 25%	D	88.63	11.89	3.78	1.63	0.56
	S_k	0.513	0.465	0.079	−0.014	−0.410

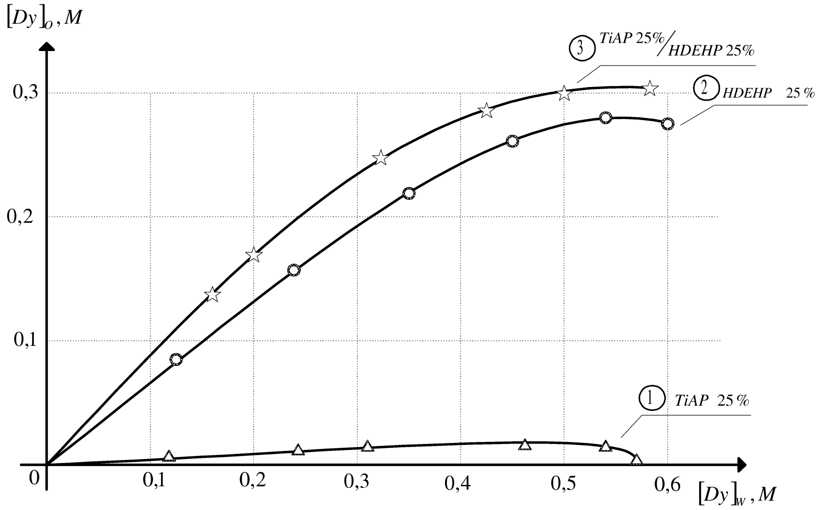

Fig. 5. Dy extraction isotherm in the $Dy(CCl_3COO)_3$–CCl_3COOH–TiAP, D2EHPA–kerosene system. TiAP 25% in kerosene, D2EHPA 25% in kerosene, mixture of TiAP 25%+D2EHPA 25% in kerosene.

ing conditions: $Dy(CCl_3COO)_3$ concentration was 0.56 M and CCl_3COOH concentration was 1 M. The dependence of Dy concentration in the organic phase on its concentration in the aqueous phase is presented in Fig. 5.

Table 4
Influences of the TiAP–D2EHPA ratio on effects of synergistic extraction

TiAP–D2EHPA ratio	Solvent		Dy	Y
3:1	TiAP	D	7.2×10^{-2}	3.8×10^{-2}
	D2EHPA	D	1.02	1.25
	Mixture	D	2.34	1.68
		S_K	0.331	0.115
2:1	TiAP	D	4.6×10^{-2}	2.2×10^{-2}
	D2EHPA	D	1.58	2.05
	Mixture	D	3.45	2.78
		S_K	0.327	0.134
1:1	TiAP	D	4.8×10^{-3}	0.3×10^{-2}
	D2EHPA	D	4.07	8.71
	Mixture	D	11.89	20.25
		S_K	0.465	0.366
1:2	TiAP	D	1.9×10^{-3}	1×10^{-3}
	D2EHPA	D	13.7	31.38
	Mixture	D	29.6	42.87
		S_K	0.335	0.136
1:3	TiAP	D	0.6×10^{-3}	0.5×10^{-3}
	D2EHPA	D	17.38	67.0
	Mixture	D	41.46	74.55
		S_K	0.378	0.046

4. Conclusion

The extraction behavior of rare earth elements with TiAP from the media of CCl_3COOH and HNO_3 was studied. This included investigating the dependence of the Yttrium distribution ratio on the nature of a Cl-substituted acetic acid in aqueous solution, the distribution regularity of rare earth elements between two phases, the influence of the salting-out agent concentration on the distribution ratio and the extraction isotherm of rare earth elements.

For the first time, the synergistic extraction of some rare earth elements in the $Ln(CCl_3COO)_3$–CCl_3COOH–TiAP, D2EHPA–kerosene system was investigated. Synergistic extraction of some rare earth elements in the trichloroacetic acid and nitric acid solutions were studied. The effects of synergistic extraction were recognized to be quiet strong in low trichloroacetic acid solution and strong nitric acid solution. The influence of factors on the synergistic extraction ratio was investigated in the above

Table 5
Influence of total concentration of extractants

		Concentration of TiAP and D2EHPA (%)			
		25	40	50	70
TiAP[a]	D	0.52×10^{-3}	1.9×10^{-3}	4.8×10^{-3}	6.5×10^{-3}
D2EHPA[a]	D	0.86	2.38	4.07	15.62
TiAP, D2EHPA	D	0.89	4.15	11.89	54.55
	S_K	0.015	0.241	0.465	0.543

[a] Concentration of each extractant is equal to 50% of total extractant concentration in the organic phase.

Table 6
Influence of the ordinal atomic number of rare earth elements on the effects of synergistic extraction

Extractant		Ln				
		La	Nd	Eu	Tb	Dy
TiAP 25%	*D*	0.0007	0.016	0.012	0.010	0.005
D2EHPA 25%	*D*	0.87	1.94	2.96	3.53	4.07
TiAP 25% + D2EHPA 25%	*D*	1.04	2.70	4.24	5.84	11.89
	S_K	0.074	0.140	0.150	0.217	0.465

systems, such as the influence of the TiAP–D2EHPA ratio, the influence of the total concentration of two extracting agents, the influence of the ordinal atomic number of rare earth elements and the influence of trichloroacetic acid and nitric acid concentrations. The Dysprosium extraction isotherm was established using TiAP and D2EHPA alone and a then mixture of these two extractants in trichloroacetic acid solutions.

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