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Synergistic Solvent Extraction and Separation of Lanthanides Using Mixtures of 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one and Aliquat-336: Influence of the Ammonium Salt Anion

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**Synergistic Solvent Extraction and
Separation of Lanthanides Using Mixtures of
1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one
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Ammonium Salt Anion**

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ABSTRACT

The synergistic solvent extraction of lanthanide ions with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HP) and the quaternary ammonium salt Aliquat 336 in chloride (QCl) or perchlorate (QClO₄) forms in C₆H₆ was studied. The composition of the extracted species was determined as Q[LnP₄] (Q⁺ is a quaternary ammonium salt cation). The values of the equilibrium constant were calculated. The extraction mechanism as well as the effect of the quaternary ammonium salt anion (Cl⁻ or ClO₄⁻) on the extraction process are discussed. The separation

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factors of the lanthanide ions were determined on the basis of the experimental data. Some trends in the lanthanide separation were established.

Key Words: Solvent extraction; 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone; Quaternary ammonium salt; Lanthanides separation factors.

INTRODUCTION

Solvent extraction is one of the most efficient methods for separation technology because of its simplicity, speed, and applicability to both tracer and macro amounts of metal ions. As there are a number of different solvent extraction systems that could be used for metal ions separation, synergistic extraction systems have received attention for a long time. The synergistic solvent extraction of multicharged transition ions,^[1-3] as well as lanthanide and actinide ions^[4-15] has been extensively studied using various acidic chelating agents, e.g., β -diketones and high molecular weight amines, amine salts, and quaternary ammonium salts as synergists. It has been found that the metal ions can be extracted synergistically with considerable enhancement. In most cases the separation of the lanthanides has also been discussed. Because of the chemical similarities of the lanthanides and the existence of these metal ions in essentially one oxidation state, the separation of the individual members is a difficult problem. The chemistry and the methods of the lanthanide separation have been thoroughly reviewed by Nash and Jensen.^[16]

As a part of the systematic study of the synergistic solvent extraction and separation of the lanthanide ions (with exception of the radioactive Pm and Ce and Pr studied previously),^[17,18] the extraction of 12 lanthanides with 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one in the presence of the quaternary ammonium salt Aliquat 336 in chloride and perchlorate forms in C_6H_6 was investigated.

EXPERIMENTAL

Reagents

Aliquat 336 (methyltrialkyl(C_8-C_{10}) ammonium chloride, QCl) was obtained from Fluka (Switzerland). The quaternary ammonium salt was purified before use according to the procedure suggested by Goto.^[19] The chloride form of the salt was transformed into the perchlorate form ($QClO_4$)



by equilibrating twice with 0.5 M solution of NaClO₄. The commercial product 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HP) with a purity higher than 99% (Fluka, Switzerland) was used as received. The diluent was benzene (Merck, Germany). The stock solutions of the lanthanide ions were prepared from their oxides (Fluka, Puriss.). Arsenazo III (Fluka, Switzerland) was of analytical grade purity as were the other reagents used.

Procedure

The experiments were carried out using 10 cm³ volumes of aqueous and organic phases. The samples were shaken mechanically for 60 minutes at room temperature, which was sufficient to reach equilibrium. After the separation of the phases, the lanthanide ion concentration in the aqueous phase was determined photometrically using Arsenazo III.^[20] The acidity of the aqueous phase was measured by a pH meter with accuracy of 0.01 pH unit. The ionic strength was maintained at 0.1 M with (Na, H)Cl, ClO₄. The initial concentration of the lanthanide ions was 2.5 × 10⁻⁴ mol/dm³ in all experiments.

RESULTS AND DISCUSSION

The solvent extraction of lanthanides with a solution of HP in C₆H₆ was studied previously.^[21] The extraction of the metal ions can be represented by the equation



where Ln denote lanthanides and “aq” and “o”, aqueous and organic phase, respectively.

The synergistic extraction of the lanthanides was studied using the traditional “slope analysis” method, permitting us to obtain both stoichiometric and equilibrium constant information about the extraction process. It is based on an examination of the variation of D_{P,Q} (the distribution coefficient due to the synergistic effect) as a function of the relevant experimental variables. As the lanthanide extraction with the quaternary ammonium salt was negligible under the experimental conditions of the present study, the values of the distribution coefficient D obtained experimentally were the sum of D_{P,Q} and D_P (due to the lanthanide extraction with HP alone under the same experimental conditions). So, the values of D_{P,Q} were calculated as log D – log D_P. Double logarithmic plots of D_{P,Q} vs. one of the variables



$[H^+]$, $[HP]$, and $[QCl (QClO_4)]$, keeping the other two constant, indicate the stoichiometry of the extractable complex and lead to the derivation of a suitable equilibrium expression and then to the calculation of the equilibrium constant. If the concentration of the extractants is constant and hydrolysis in the aqueous phase as well as polymerization in the organic phase occur to a negligible extent only, then the plots will be straight lines and their slopes will give the number of the ligands.

The experimental data for the extraction of 12 lanthanide ions with mixtures of HP and QCl ($QClO_4$) are shown in Figs. 1–6.

The plots of $\log D_{P,Q}$ vs. pH and $\log [HP]$ are linear with slopes close to 4, and the plots of $\log D_{P,Q}$ vs. $\log [QCl (QClO_4)]$ are linear and exhibit slopes close to 1 for all lanthanides.

On the basis of the slope analysis data, the synergistic extraction of the lanthanides can be described by the following reaction



where $A^- = Cl^-$ or ClO_4^- .

The overall equilibrium constant $K_{P,Q}$ can be determined by the equation

$$\log K_{P,Q} = \log D_{P,Q} - 4 \log [HP] - \log [QA] - 4pH + \log [A^-] \quad (3)$$

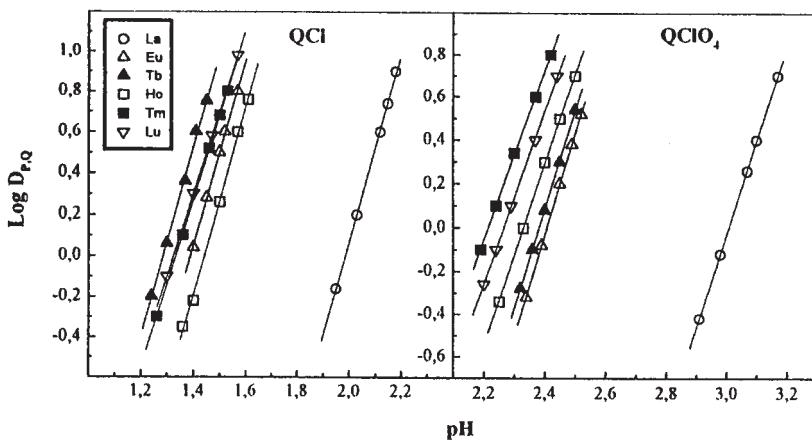


Figure 1. $\log D_{P,Q}$ vs. pH for the extraction of lanthanide elements having odd atomic number with HP–QCl and HP– $QClO_4$ mixtures at $[HP] = 4 \times 10^{-2} \text{ mol}/\text{dm}^3$, $[QCl] = 5 \times 10^{-3} \text{ mol}/\text{dm}^3$, and $[QClO_4] = 3.7 \times 10^{-3} \text{ mol}/\text{dm}^3$.



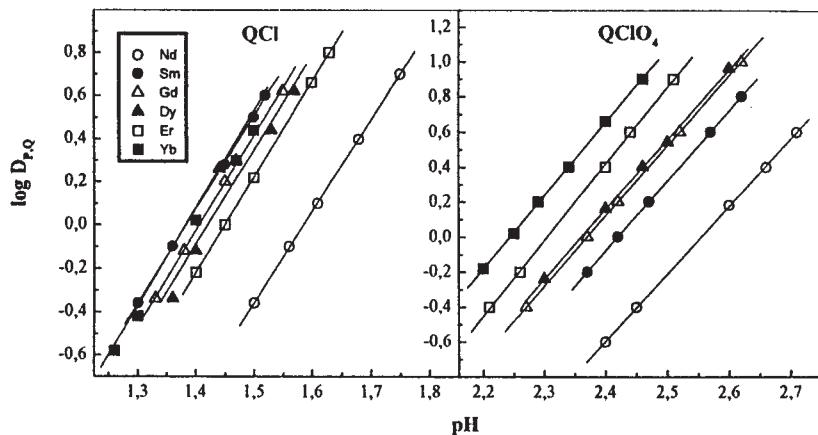


Figure 2. Log $D_{p,Q}$ vs. pH for the extraction of lanthanide elements having even atomic number with HP-QCl and HP- QClO_4 mixtures at $[\text{HP}] = 4 \times 10^{-2} \text{ mol}/\text{dm}^3$, $[\text{QCl}] = 5 \times 10^{-3} \text{ mol}/\text{dm}^3$, and $[\text{QClO}_4] = 3.7 \times 10^{-3} \text{ mol}/\text{dm}^3$.

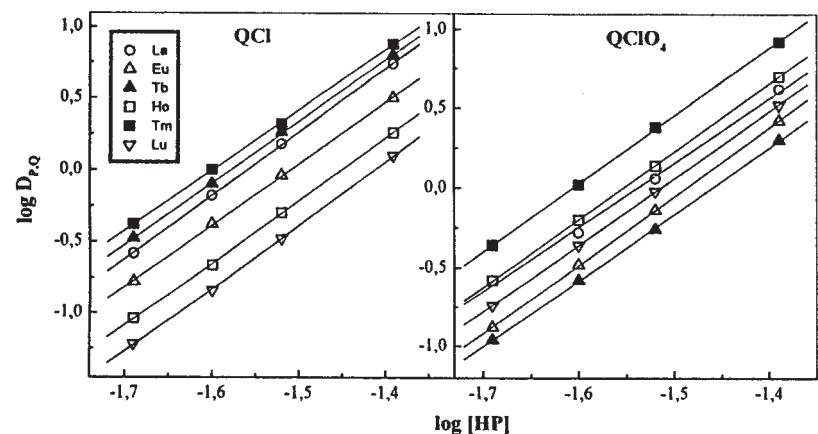


Figure 3. Log $D_{p,Q}$ vs. $\log [\text{HP}]$ for extraction of lanthanide elements having odd atomic number with HP-QCl and HP- QClO_4 mixtures at $[\text{QCl}] = 5 \times 10^{-3} \text{ mol}/\text{dm}^3$ and $[\text{QClO}_4] = 3.7 \times 10^{-3} \text{ mol}/\text{dm}^3$. QCl: La, pH = 2.15; Eu, pH = 1.50; Tb, pH = 1.45; Ho, pH = 1.50; Tm, pH = 1.55; Lu, pH = 1.35. QClO_4 : La, pH = 3.15; Eu, pH = 2.50; Tb, pH = 2.45; Ho, pH = 2.50; Tm, pH = 2.45; Lu, pH = 2.40.



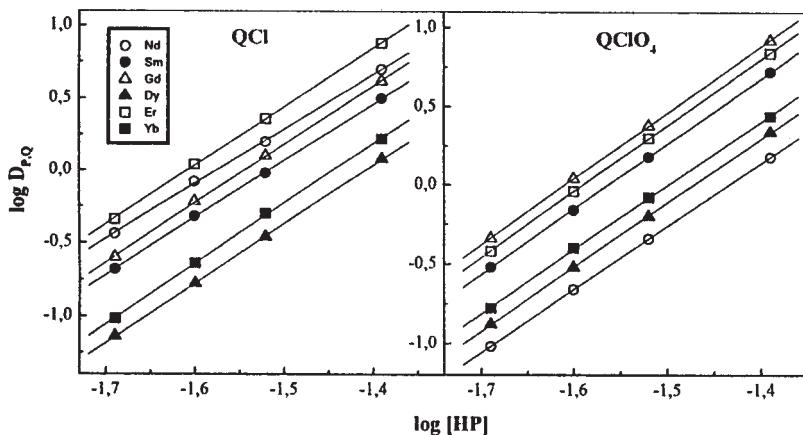


Figure 4. Log $D_{P,Q}$ vs. $\log [HP]$ for the extraction of lanthanide elements having even atomic number with HP-QCl and HP-QClO₄ mixtures at $[QCl] = 5 \times 10^{-3}$ mol/dm³ and $[QClO_4] = 3.7 \times 10^{-3}$ mol/dm³. QCl: Nd, pH = 1.75; Sm, pH = 1.50; Gd, pH = 1.55; Dy, pH = 1.45; Er, pH = 1.65; Yb, pH = 1.45. QClO₄: Nd, pH = 2.60; Sm, pH = 2.60; Gd, pH = 2.60; Dy, pH = 2.45; Er, pH = 2.50; Yb, pH = 2.35.

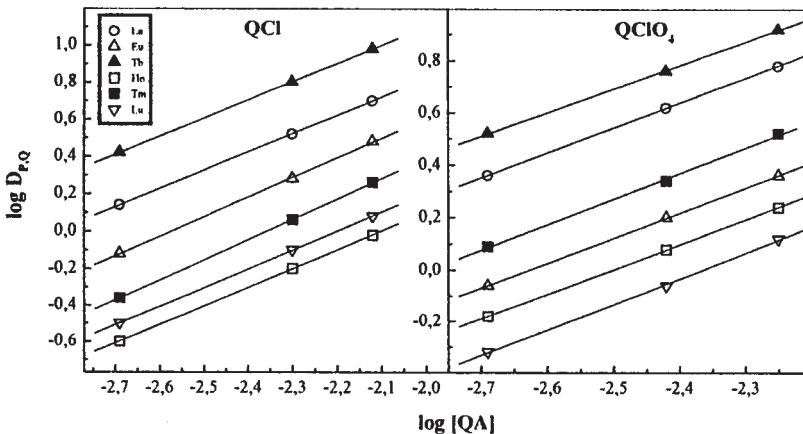


Figure 5. Log $D_{P,Q}$ vs. $\log [QCl, QClO_4]$ for extraction of lanthanide elements having odd atomic number with HP-QCl and HP-QClO₄ mixtures at $[HP] = 4 \times 10^{-2}$ mol/dm³. QCl: La, pH = 2.10; Eu, pH = 1.45; Tb, pH = 1.45; Ho, pH = 1.40; Tm, pH = 1.35; Lu, pH = 1.30. QClO₄: La, pH = 3.15; Eu, pH = 2.45; Tb, pH = 2.55; Ho, pH = 2.35; Tm, pH = 2.30; Lu, pH = 2.25.



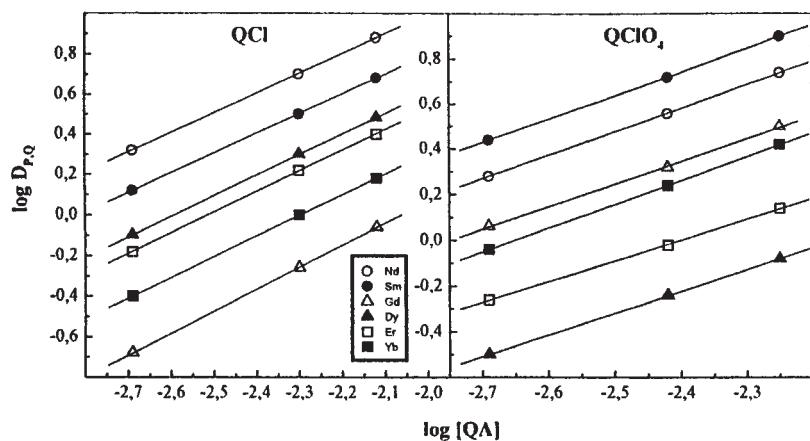
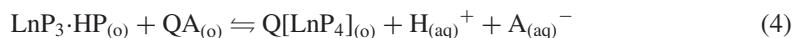


Figure 6. Log $D_{P,Q}$ vs. $\log [QCl, QClO_4]$ for extraction of lanthanide elements having even atomic number with HP-QCl and HP-QClO₄ mixtures at $[HP] = 4 \times 10^{-2} \text{ mol/dm}^3$. QCl: Nd, pH = 1.75; Sm, pH = 1.50; Gd, pH = 1.35; Dy, pH = 1.50; Er, pH = 1.50; Yb, pH = 1.40. QClO₄: Nd, pH = 2.70; Sm, pH = 2.60; Gd, pH = 2.45; Dy, pH = 2.30; Er, pH = 2.30; Yb, pH = 2.30.

The formation of mixed adducts in the organic phase can be expressed by the equation



The equilibrium constant $\beta_{P,Q}$ for the organic phase synergistic reaction can be determined as

$$\log \beta_{P,Q} = \log K_{P,Q} - \log K_P \quad (5)$$

The values of $\log K_P$, $K_{P,Q}$, and $\beta_{P,Q}$ are given in Table 1. The equilibrium constants are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions, i.e., they are concentration constants. The variations in $\log K_{P,Q}$ with the atomic number of the lanthanides are given in Fig. 7. It is seen from the figure that the $\log K_{P,Q}$ values change in almost the same manner with increasing atomic number for both HP-QCl and HP-QClO₄ combinations. It can be concluded that the change of the quaternary ammonium salt anion (Cl^- with ClO_4^-) produces only quantitative differences in the synergistic extraction of the lanthanide ions. The great decrease of the $\log K_{P,Q}$ values (3.5 to 4 orders) caused by the change of the anion of the salt is similar to those found for the lanthanide extraction with thenoyltrifluoroacetone (HTTA) and QCl (QClO₄)



Table 1. Values of the equilibrium constants K_p , $K_{p,q}$, and $\beta_{p,q}$ for the lanthanide extraction with HP-QCl ($QClO_4$) mixtures in C_6H_6 and the separation factors of lanthanides.

Ln^{3+}	$\log K_p^{[21]}$	HP-QCl			HP- $QClO_4$		
		$\log K_{p,q}$	$\log \beta_{p,q}$	S.F.	$\log K_{p,q}$	$\log \beta_{p,q}$	S.F.
La	-5.26	-0.97	4.29	—	-5.00	0.26	—
Ce	-4.35	-0.12	4.23	7.08	-4.05	0.30	8.91
Pr	-4.08	0.36	3.60	3.02	-3.88	0.20	1.47
Nd	-3.50	0.59	4.09	1.69	-3.25	0.25	4.29
Sm	-3.12	1.29	4.41	5.01	-2.69	0.43	3.63
Eu	-2.99	1.32	4.31	1.07	-2.62	0.37	1.17
Gd	-3.04	1.41	4.45	1.23	-2.53	0.51	1.23
Tb	-2.80	1.67	4.47	1.81	-2.47	0.33	1.14
Dy	-2.76	1.25	4.01	0.38	-2.43	0.33	1.09
Ho	-2.69	1.22	3.91	0.93	-2.26	0.43	1.47
Er	-2.64	1.19	3.83	0.93	-2.16	0.48	1.25
Tm	-2.42	1.20	3.62	1.02	-1.84	0.58	2.08
Yb	-2.13	1.25	3.38	1.12	-1.93	0.19	0.81
Lu	-2.19	1.13	3.32	0.75	-2.04	0.15	0.77

Notes: Error limits in the range of $\leq \pm 0.08$; S.F. = separation factors.

mixtures.^[14] Because of the formation of the same type of anionic complex in both cases, the effect of the anion of the quaternary ammonium salt on the synergistic extraction process can be explained in the same manner: the bond in $QClO_4$ is stronger than that in QCl ^[22] and the formation of the complexes $Q[LnP_4]$ upon breaking the bond between the cation and the anion of the salt is more difficult in the presence of $QClO_4$. On the other hand, when primary, secondary, or tertiary alkylammonium salts were used as synergistic agents,^[6,23] the salt anion caused small effects on the lanthanide extraction because in these cases, adduct chelates $Ln(TTA)_3BHA$ (BHA is the alkylammonium salt) were extracted. In such complexes, the ammonium salt is bound to the metal ion through its anion,^[24] i.e., complex formation is not connected with breaking of the bond between the cation and the anion of the salt.

Mixed anionic complexes of the type $Q[M^{n+}L_{n+1}]$ (L^- is a chelating ligand) were established earlier for lanthanide and some di- and trivalent metal ions synergistic extraction but two different opinions about the synergistic agent were expressed. Some investigators^[1-3,10-13] suggested that the synergist is not the quaternary ammonium salt but the compound obtained by the interaction of the chelating extractant and the quaternary ammonium salt, i.e., the synergist is the compound of the type Q^+L^- . The fact that such



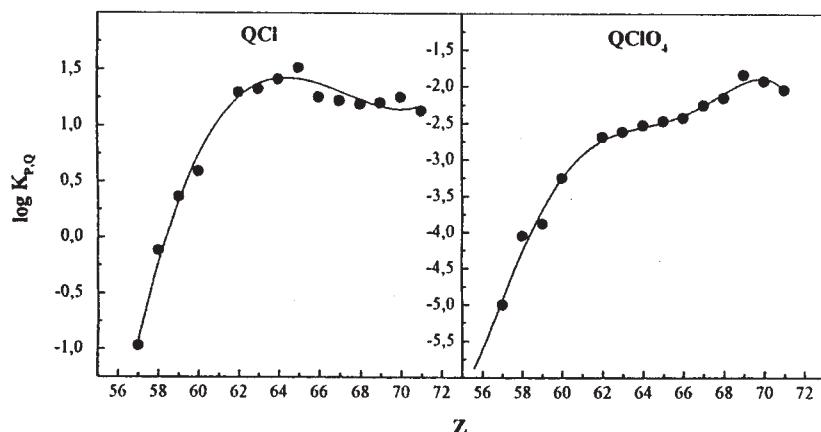


Figure 7. Variation of $\log K_{P,Q}$ with atomic number (Z).

a compound has a larger size than the other ligands (L^-) taking part in the complex $Q[M^{n+}L_{n+1}]$, and that it will be sterically hindered to attach itself to the metal ion, has not been commented on. On the other hand, Dukov et al.^[4-6] and Freiser et al.^[7,8] accept that the synergistic agent is the quaternary ammonium salt.

The role of the interaction of the extractants HP and QCl or $QClO_4$ on the synergistic extraction was studied by Dukov et al.^[21] It was found that under the conditions of the lanthanide synergistic extraction, the interaction between the extractants is low.

Interesting results concerning the influence of the extractants interaction on the synergistic extraction process have been published earlier by Ke and Li.^[24] They studied adduct formation between the chelate $Cu(TTA)_2$ and alkylamines (B), alkylammonium salts (BHCl), as well as with the compounds B.HTTA and BHCl.HTTA obtained by extractants pre-equilibration. It was established that the copper chelate forms the mixed adduct $Cu(TTA)_2BHCl$ in the presence of alkylammonium salt, but the adduct $Cu(TTA)_2B$ is formed to a much smaller extent in the presence of alkylamines. Formation of mixed adducts with the compounds B.HTTA and BHCl.HTTA was not found.

The unfavorable role of the extractant interaction was also noted by Zhang.^[25] The investigator concluded that the antagonistic effect found for the extraction of Pd(II) with mixtures of 1-phenyl-3-methyl-4-propionyl-pyrazol-5-one and a tertiary alkylamine can be explained by a decrease of the pyrazolone concentration in the organic phase due to an interaction between the extractants. As far back as 30 years ago, Marcus and Kertes^[26] also pointed



out that the interaction between an acidic and neutral extractant is a reason for the destruction of the synergism.

Taking into account these considerations, it could be concluded that when metal ions are extracted with mixtures of chelating extractants and alkylammonium salts, two competitive reactions can occur, i.e., formation of mixed complexes (no interaction between the extractants) producing synergism and interaction between the extractants producing ion-pair formation. It could be suggested that when synergism is observed, the bonds in the mixed complex have to be stronger than those in the ion-pair Q^+L^- . Then, according to the Le Chatelier's principle the equilibrium connected with the ion-pairs Q^+L^- formation will be shifted to the left and the ion-pairs (as far as they are formed) will be destroyed. In the opposite case, antagonism will occur.

The separation of the lanthanide ions using HP-QCl and HP-QClO₄ mixtures can be assessed by the separation factors (SF) calculated as the ratio of the distribution coefficients of two adjacent lanthanides. When the metal ions form complexes of the same type (as in the present case), the separation factors can be determined as the ratio of the equilibrium constants $K_{P,Q}$. The values of the separation factors are given in Table 1. The data show that the separation factors between adjacent metal ions for the first few lanthanides are rather high. The change of the anion of the quaternary ammonium salt hardly influences the lanthanide separation. The same was found earlier for the extraction of lanthanides with HTTA alone and with mixtures of HTTA-QCl and HTTA-QClO₄.^[14] The data in Table 1 do not show a noticeable relation between the extractants affinity for the lanthanide ions and the separation factors. To establish the influence of the increased extraction of ions on their separation, the separation factors of the pairs La-Lu, La-Eu, and Eu-Lu for HP alone or in mixture with QCl and QClO₄ were calculated. The data are given in Table 2. It is seen that the separation factors decrease in the order HP > HP-QClO₄ > HP-QCl until the lanthanide extraction increases in the

Table 2. Tendencies in the separation of the lanthanides in their solvent extraction with HP alone and with HP-QCl and HP-QClO₄ mixtures.

Extractant	Separation factors		
	La-Lu	La-Eu	Eu-Lu
HP ^[21]	1.2×10^3	186.1	6.3
HP-QClO ₄	910	240	3.8
HP-QCl	125.3	194	1.55



opposite order. The same tendency (with small exceptions) was established for lanthanides extraction with HTTA alone and in mixtures with QCl and QClO_4 . It is interesting to note that HTTA, which is much poorer extractant for lanthanides than HP (the values of the equilibrium constants are 4 to 5 orders of magnitude lower),^[14,21] exhibits a separation for the pairs La–Lu, La–Eu and Eu–Lu, which is 4.6, 3.6, and 1.3 times higher than those obtained when HP is used as the extractant.

CONCLUSION

Lanthanide ions are synergistically extracted by HP–QCl (QClO_4) mixtures as $\text{Q}[\text{LnP}_4]$ species. The anion of the quaternary ammonium salt exerts a considerable influence on the lanthanide extraction. The great decrease of the equilibrium constant values (3.5 to 4 orders of magnitude) caused by the change of the anion of the salt (Cl^- with ClO_4^-) is explained by the difference of the bond energy in QCl and QClO_4 .

The separation factors between the adjacent metal ions are not high for both HP–QCl and HP– QClO_4 systems. The experimental data show that the lanthanide extraction using HP alone and mixtures of HP and QCl or QClO_4 increases in the order $\text{HP} < \text{HP–QClO}_4 < \text{HP–QCl}$ but the separation factors decrease in that order.

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