Benzo-15-Crown-5 as Synergistic Agent in the Extraction of Pr(III) from Perchlorate Medium with Thenoyltrifloroacetone in 1,2-Dichloroethane, Carbon Tetrachloride and Chloroform

Valeri Jordanov

Department of General and Inorganic Chemistry, University of Chemical Technology and Metallurgy, 8 Kliment Okhridski Blvd., 1756 Sofia, Bulgaria

* Corresponding author: E-mail: val_bgm @abv.bg

Abstract

The synergistic solvent extraction of Praseodymium (Pr) from perchlorate medium by mixtures of thenoyltrifluoroacetone (HTTA) and a crown ether benzo-15-crown-5 (B15C5) is studied. The composition of the extracted species has been determined as $Pr(TTA)_3.2B15C5$. The values of the equilibrium constant $K_{T,S}$ are calculated. Furthermore, the influence of the polarity of organic diluents on the extraction process is investigated.

Keywords: synergistic extraction, lanthanides, thenoyltrifluoroacetone, benzo-15-crown-5.

1. Introduction

The chelating extractant thenoyltrifluoroacetone has been extensively studied in the extraction of lanthanides alone[1,2] or in mixtures with various synergistic agents.[3–8]

In the last 15–20 years, crown ethers (CE) have been often used as synergistic agents. Extraction of trivalent lanthanides,[9–20] divalent transition and alkali metals[21,22] with mixtures of HTTA or other chelating extractants and different CE have been investigated. It was found out that both the crown ether type and its concentration influence the complexes' stoichiometry.[10–12] Using synergistic agents having high basicity and concentration results in formation of complexes-M(TTA)₃.2CE, while M(TTA)₃.CE has been obtained in low basicity and concentration of CE (M=Ln).
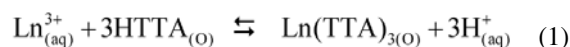
The ionic medium and the ionic strength in the aqueous phase as well as the polarity of the organic diluents influence the extracted complex species, too.[13–16] Extraction of metals from NO_3^--medium in organic phase containing polar diluents usually results in the formation of ionic type complex $-[M(TTA)_2CE]^+(NO_3)^-$. On the other hand, throughout the extraction from Cl^- medium in low polar diluents, metals form adducts – M(TTA)₃.nCE (n = 1 or 2). The two types of complexes have been established during the extraction of *f*-elements from ClO_4^-–medium.

In the present work, the extraction of Praseodymium (Pr) from perchlorate medium with mixtures of HTTA and B15C5 is studied.

2. Results and Discussion

The solvent extraction of lanthanides with HTTA alone in C_6H_6 is studied by Poskanzer and Foreman.[1] It has been found out that metal extraction can be expressed by

$$Ln^{3+}_{(aq)} + 3HTTA_{(O)} \rightleftarrows Ln(TTA)_{3(O)} + 3H^+_{(aq)} \quad (1)$$

$$K_T = \frac{[Ln(TTA)_3]_{(O)}.[H^+]^3_{(aq)}}{[Ln^{3+}]_{(aq)}.[HTTA]^3_{(O)}} \quad (2)$$

$$D_T = \frac{[Ln(TTA)_3]_{(O)}}{[Ln^{3+}]_{(aq)}} \quad (3)$$

where D_T denotes the distribution coefficient, Ln – lanthanides, and "aq" and "o" denote the aqueous and organic phase, respectively.
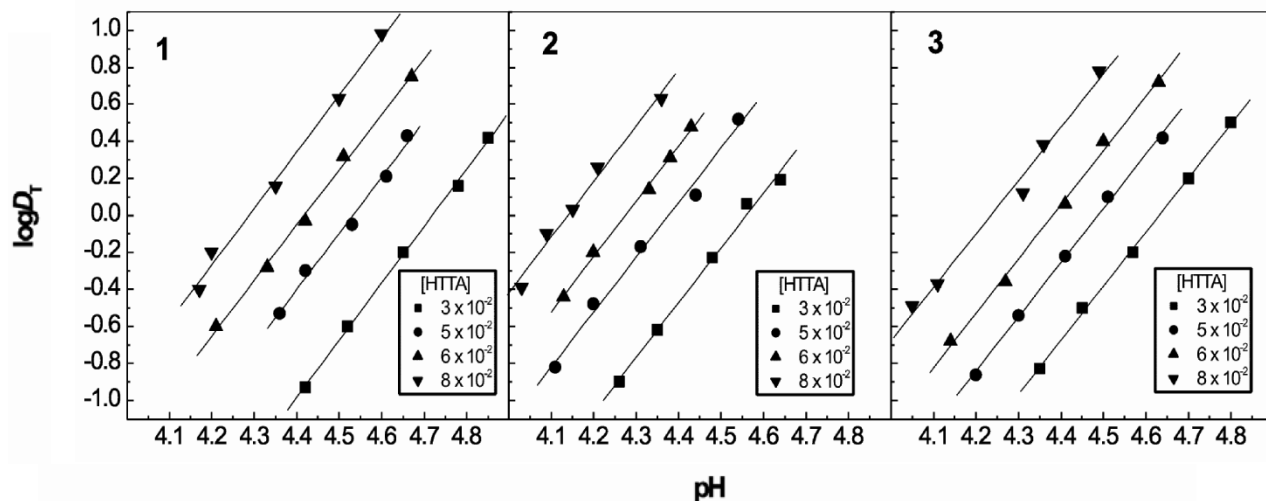
Figure 1. Log D_T vs. pH for Pr extraction with HTTA. 1- CCl_4; 2- $C_2H_4Cl_2$; 3- $CHCl_3$

Later the same type of complexes have been obtained in metals extraction with HTTA in other organic diluents, too.[2,3]
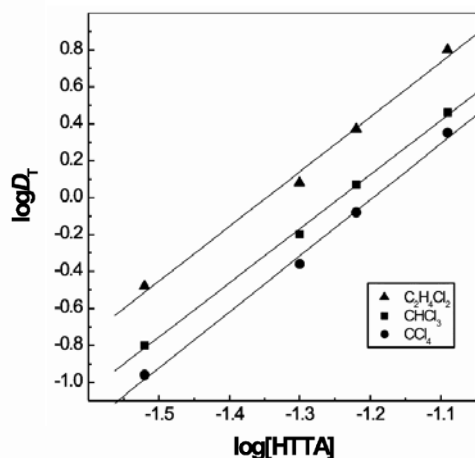

Figure 2. Log D_T vs. [HTTA] for Pr extraction at pH = 4.40

Table 1. Values of the equilibrium constant for Pr extraction with HTTA alone and with mixtures of HTTA and B15C5

Diluent	$\log K_T$	$\log K_{T,S}$	$\log \beta_{T,S}$
CCl_4	-9.65 ± 0.03	-1.89 ± 0.03	7.76 ± 0.06
$CHCl_3$	-9.45 ± 0.04	-2.89 ± 0.04	6.56 ± 0.08
$C_2H_4Cl_2$	-9.16 ± 0.03	-3.47 ± 0.04	5.69 ± 0.07

In the present study, the extraction of Pr with HTTA from perchlorate medium in 1,2-dichloroethane ($C_2H_4Cl_2$), carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) is investigated. The experimental data about the distribution coefficient D_T vs. pH and [HTTA] are shown in Fig.1 and 2. The values of equilibrium constant K_T for metal chelates formation are given in Table 1.

Alone, the Pr extraction with B15C5, is negligible under the experimental conditions of the present research.

The synergistic solvent extraction of Pr is studied by an examination of the variation of $D_{T,S}$ (the distribution coefficient caused by the synergistic effect) with relevant experimental variables. If the extractants' concentration is
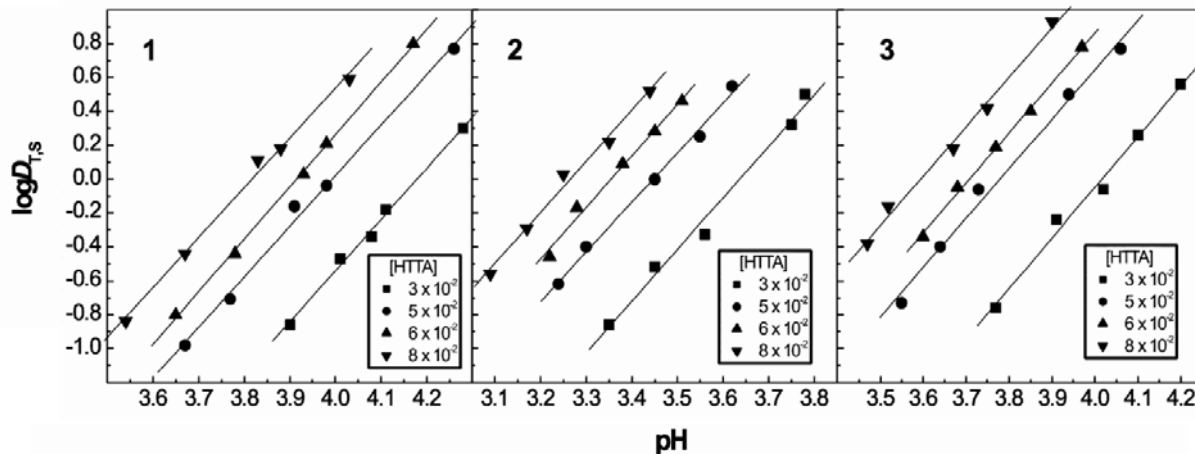

Figure 3. Log $D_{T,S}$ vs. pH for Pr extraction with HTTA and B15C5 at [B15C5] = $5 \cdot 10^{-3}$ mol dm^{-3}. 1- $C_2H_4Cl_2$; 2- CCl_4; 3- $CHCl_3$

constant, and if the hydrolysis and polymerization in aqueous and organic phases, respectively, are negligible, then the plots will give the number of ligands included in the extraction complexes. Double logarithmic plots of $D_{T,S}$ vs. one of the variables pH, [HTTA] or [B15C5], retaining the other two constant are shown in Figs.3–6.
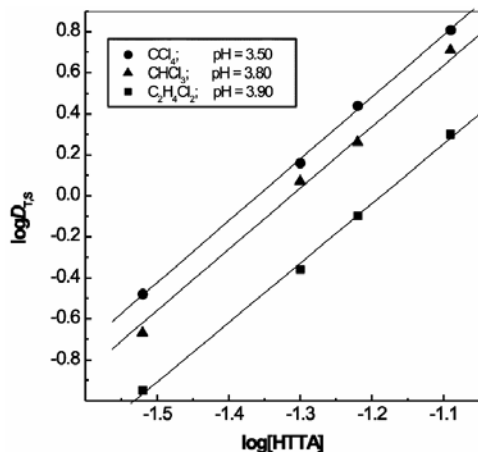

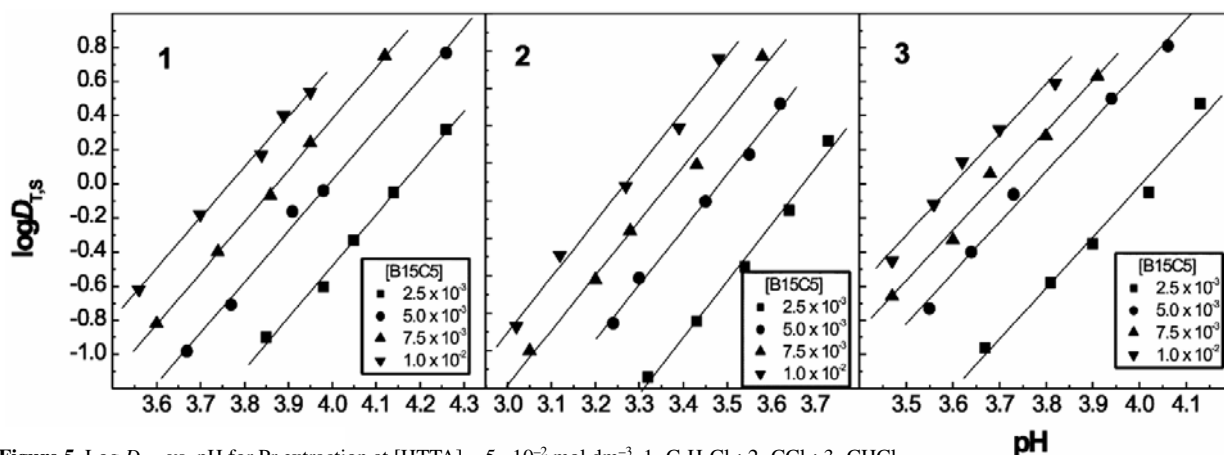**Figure 4.** Log $D_{T,S}$ vs. log.[HTTA] for Pr extraction at B15C5] = $5 \cdot 10^{-3}$ mol dm^{-3}.

The plots of log $D_{T,S}$ vs. pH and [HTTA] are linear, with slopes close to 3, and the plots of log $D_{T,S}$ vs. [B15C5] show slopes close to 2.

On the basis of slope analysis data, the synergistic extraction of Pr can be described by the equation

$$Pr_{(aq)}^{3+} + 3HTTA + 2S_{(O)} \leftrightarrows Pr(TTA)_3 \cdot 2S_{(O)} + 3H_{(aq)}^+ \quad (4)$$
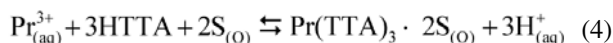
where S denotes B15C5.

The equilibrium constant $K_{T,S}$ for the synergistic complex formation can be shown as follows:

$$\log K_{T,S} = \log D_{T,S} - 3\log[HTTA] - 2\log[S] - 3pH \quad (5)$$

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

$$Pr(TTA)_{3(O)} + 2S_{(O)} \leftrightarrows Pr(TTA)_3 \cdot 2S_{(O)} \quad (6)$$

The equilibrium constant $\beta_{T,S}$ for the synergistic reaction in the organic phase can be determined as

$$\log \beta_{T,S} = \log K_{T,S} - \log K_T \quad (7)$$

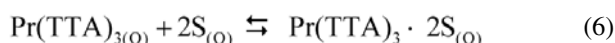**Figure 5.** Log $D_{T,S}$ vs. pH for Pr extraction at [HTTA] = $5 \cdot 10^{-2}$ mol dm^{-3}. 1- C$_2$H$_4$Cl$_2$; 2- CCl$_4$; 3- CHCl$_3$

Figure 6. Log $D_{T,S}$ vs. log.[B15C5] for Pr extraction at [HTTA] = $5 \cdot 10^{-2}$ mol dm^{-3}.

The values of log $K_{T,S}$ and $\beta_{T,S}$ 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 experimental conditions, i.e. they are concentration constants.

The data in Table 1 shows that the values of log $K_{T,S}$ and $\beta_{T,S}$ decrease with increasing of the dielectric constant of organic diluents. That can be explained by the possibility of hydrogen-bonding formation due to interaction between extractants and polar diluents.

In the extraction of trivalent lanthanides and actinides from ClO$_4^-$ -medium with HTTA and DCH18C6 into 1,2-dichloroethane by Katatsuji et al. ionic complexes [M(TTA)$_2$ DCH18C6]$^+$ClO$_4^-$ are obtained.[13] Complexes in which the anion of the aqueous phase is a part of the extracted species-M(X)(L$_2$).CE have also been formed in the
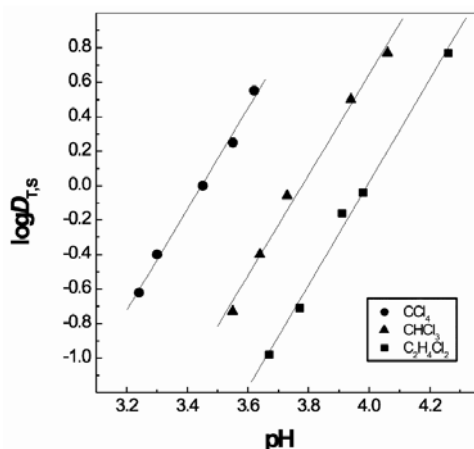
Figure 7. Log $D_{T,S}$ vs. pH for Pr extraction at [HTTA] = 5 · 10^{-2} mol dm^{-3} and [B15C5] = 5 · 10^{-3} mol dm^{-3}.

extraction of light lanthanides with others β-diketones into polar diluents.[14–16] On the contrary, adducts M(L$_3$).CE have been registered in non-polar medium (M=Ln, L=β-diketones and CE=18C6, DB18C6 or DCH18C6).[9–11] In our case, the change of diluents' polarity results in considerable variation of the value of the distribution coefficient $D_{T,S}$ (fig.7). No possibility for changes in the composition of the synergistic complexes is confirmed.[20]

Lakkis et al. have obtained ionic type complex (KCE)$^+$.M(PMBP)$_3^-$ in the extraction of Co(II) and Ni(II) with mixture of 1-phenyl-3- methyl-4- benzoylpyrazol-5-one and CE (18C6 or DCH18C6) from aqueous phase containing 1 mol dm^{-3} KClO$_4$.[21] On the other hand, adducts M(PMBP)$_2$.CE from 1 mol dm^{-3} LiCl or (CH$_3$)$_4$NCl medium are obtained. In our investigation, ionic type complex formation is not established in the extraction of Pr from aqueous phase containing KClO$_4$. In all experimental conditions the adduct-Pr(TTA)$_3$ 2B15C5 is obtained. In similar complexes, Mathur and Choppin admit that metal ion is bonded with only three oxygen atoms, from each B15C5.[19] There are two crown molecules, placed above and under the metal chelate plane, respectively.

3. Experimental

3. 1. Reagents

HTTA (Merck, p.a.) and B15C5 (Fluka, puriss.) were used as supplied. The stock solutions of the Pr were prepared from its oxide Pr$_6$O$_{11}$ (Fluka,puriss). Arsenazo III (Fluka) was of analytical grade purity as were the other reagents used.

3. 2. Procedure

The experiments were carried out using 10 cm^3 volumes of aqueous and organic phases. The samples were shaken mechanically for 60 min at room temperature which was sufficient to reach equilibrium. After phase separation, the concentration of Pr in the aqueous phase was determined photometrically using Arsenazo III.[23] The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0,01 pH unit. The ionic strength was maintained at 0,1 mol dm^{-3} with (K,H)ClO$_4$. The initial concentration of Pr was 2,5.10^{-4} mol dm^{-3} in all experiments.

4. Conclusions

Pr is synergistically extracted with HTTA-B15C5 mixtures as an adduct –Pr(TTA)$_3$ 2B15C5. Polarity of organic diluents causes a considerable influence on the metal extraction but not to the extracted complexes' stoichiometry. The values of distribution ratio $D_{T,S}$ decrease in the order CCl$_4$ > CHCl$_3$ > C$_2$H$_4$Cl$_2$, i.e. the synergistic extraction is greatest in the least polar diluent. Extraction from aqueous phase containing KClO$_4$, does not result in ionic type complex formation.

5. References

1. A. M. Poskanzer and B. M. Foreman, *J. Inorg. Nucl. Chem.* **1961**, *16*, 323–336.
2. J. Alstad, L.H. Augustson and L. Farbu, *J. Inorg. Nucl. Chem.* **1974**, *36*, 889–903.
3. L. Newman and P. Klotz, *Inorg. Chem.* **1972**, *11*, 2150–2154.
4. M. S. Bhatti and G. Duyckaerts, *Anal. Chim. Acta* **1983**, *149*, 369–373.
5. S. Nakamura and N. Suzuki, *Polyhedron* **1988**, *7*, 155–159.
6. I. L. Dukov and V. M. Jordanov, *Solvent Extr. Ion.Exch.* **1995**, *13*, 997–1008.
7. I. L. Dukov and V. M. Jordanov, *Solvent Extr. Ion.Exch.* **1998**, *16*, 1151–1160.
8. M. Atanassova, V. M. Jordanov and I. L. Dukov, *Hydrometallurgy* **2002**, *63*, 41–47.
9. G. M. Nair and D. R. Prabhu, *J. Radioanal. Nucl. Chem.* **1988**, *121*, 83–90.
10. Y. Meguro, H. Muto and Z. Yoshida, *Anal. Sci.* **1991**, *7*, 51–54.
11. D. D. Ensor and A. H. Shah, *J. Radioanal. Nucl. Chem. Lett.* **1988**, 127, 235–239.
12. I. L. Dukov, *Monatsh.Chem.* **1993**, *124*, 689–693.
13. Y. Kitatsuji, Y. Meguro, Z. Yoshida, T. Yamamoto and K. Nishizawa, *Solvent Extr. Ion. Exch.* **1995**, *13*, 289–300.
14. Y. Meguro, Y. Kitatsuji, T. Kimura and Z. Yoshida, *J. Alloys Compd.* **1998**, *271–273*, 790–793.
15. M. L. P. Reddy, R. L. Varma and T. R. Ramamohan, *Radiochim. Acta*, **1999**, *80*, 151–154.
16. F. A. Shehata, N. El-Hefny and H. F. Aly, *Solvent Extraction for the 21st Century, Proceedings of ISEC'99,* Barcelona, Spain, **1999 July 11–16 (publ. 2001),** *2*, 1387–1393.
17. R. Pavithran and M. L. P. Reddy, *Radiochim. Acta* **2003**, *91*, 163–168.

18. N. Yamamoto, N. Hirayama and T. Honjo, *Solvent Extr. Res. Dev. Jpn.* **1999**, *6*, 182–188.

19. J. N. Mathur and G. R. Choppin*, Solvent Extr. Ion. Exch*. **1993**, *11*, 1–9.

20. I. L. Dukov, *Solvent Extr. Ion. Exch*. **1986**, *10*, 637–653.

21. M. Lakkis, J. P. Brunette and M. J. F. Leroy, *Solvent Extr. Ion. Exch*. **1986**, *4*, 287–299

22. T. Shimosato and N. Hirayama *Solvent Extraction for the 21ˢᵗ Century, Proceedings of ISEC'99,* Barcelona, Spain, **1999 July 11–16 (publ. 2001),** *1*, 585–590.

23. S. V. Savvin: Arsenazo III, Atomizdat, Moskva, **1966**, 177–178.

Povzetek

Raziskovali smo sinergijo topil pri ekstrakciji praseodimija (Pr) iz perkloratnega medija z mešanicami tenoiltrifluoroacetona (HTTA) in crown etra benzo-15-crown-5 (B15C5). Določili smo strukturo ekstrahiranih delcev (Pr(TTA)$_3$.2B15C5), vrednosti ravnotežnih konstant $K_{T,S}$ ter vpliv polarnosti organskih topil na proces ekstrakcije.