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SOLVENT EXTRACTION OF LANTHANOID(III) IONS WITH TERNARY MIXTURES OF 4-BENZOYL-3-METHYL-1-PHENYL-2-PYRAZOLIN-5-ONE, 1-(2-THIENYL)-4,4,4-TRIFLUORO-1,3-BUTANEDIONE AND THE QUATERNARY AMMONIUM SALT ALIQUAT 336

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ABSTRACT

The synergistic solvent extraction of the lanthanoid(III) ions with a ternary mixture of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) and 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (2-thenoyltrifluoroacetone, HTTA), and the quaternary ammonium salt methyltrialkyl(C_8-C_{10})ammonium chloride (Aliquat 336,QCl) in C_6H_6 has been investigated. In the presence of a ternary mixture of extractants (HP, HTTA and QCl) extraction of an anionic complex Q[LnP_3(TTA)] was established. The values of the equilibrium constants were calculated for the extraction of La(III), Ce(III), Pr(III), Nd(III) and Sm(III). A synergistic effect was observed for the extraction of the above-mentioned ions with the ternary mixture of extractants but an antagonistic effect was found for Eu(III), Gd(III) and the heavier members of the 4f-series.

Keywords: Lanthanoids, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione, Aliquat 336, Synergistic Effect, Antagonistic Effect.

INTRODUCTION

During the last decades the synergistic extraction of a great number of metals has been studied [1-5]. In several investigations the extraction of metals with more than two extractants has been described. Chinese authors have studied the extraction of some lanthanoids with ternary [6] or quaternary [7] mixtures of extractants as well as the extraction of U(VI) with ternary mixtures [8-12]. Combinations including two chelating and one neutral or one chelating and two neutral extractants have been used. Earlier, Irving [13] has studied the extraction of Co(II) with a ternary mixture of thenoyltrifluoroacetone (HTTA), 3-methylpyridine (3-mepy) and 4-methylpyridine (4-mepy). The formation of mixed species Co(TTA)$_2$(3-mepy)(4-mepy) has been demonstrated but no additional synergism has been found. No mixed adducts involving the three extractants were found by Dukov and Genov [14] when Pr(III) was extracted with HTTA, trioctylamine (TOA) and Aliquat 336. On the contrary, D'Olieslager et al. [15] have found both mixed complex formation and an additional synergism for the extraction of Tm(III) with a ternary mixture of benzoyltrifluoroacetone, tributylphosphate and dibutylbutylphosphonate. Sekine and Dyrssen [16] have established that the extraction of Eu(III) with a mixture of HTTA, isopropyltropolone (IPT) and tributylphosphate (TBP) has caused formation of the

complexes $Eu(TTA)_2(IPT)(TBP)_2$ or $Eu(TTA)(IPT)_2(TBP)_2$.

In the present paper the solvent extraction of the metals of the lanthanoid series with ternary mixtures of thenoytrifluoroacetone (HTTA) and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) and Aliquat 336 (QCl) in benzene was investigated.

EXPERIMENTAL

Reagents and Solutions

The commercial compounds HP with purity > 99%(Fluka, Switzerland) and HTTA (Merck, Germany, p.a.) were used as supplied. Aliquat 336 (methyltrialkyl(C_8-C_{10}) ammonium chloride, QCl) was obtained from Fluka. The quaternary ammonium salt was purified before using it according to the procedure suggested by Goto [17]. Benzene (Merck, Germany, p.a.) was used as a diluent. Arsenazo III (Fluka, Switzerland) was of analytical grade purity. The initial aqueous solutions of the lanthanoid(III) metals were prepared by dissolving their oxides (Fluka, Switzerland, puriss) in concentrated HCl and subsequent dilution by distilled water. The initial metal ion concentration was maintained at 2.5×10^{-4} mol dm^{-3} for all experiments. The ionic strength was maintained at 0.1M with (Na, H) Cl.

Distribution Experiments

Equal volumes (10 cm^3) of the aqueous and the organic phases were shaken in a mechanical shaker for 1 hour at room temperature ($20^oC \pm 2^oC$). After separation of the phases, the lanthanoid content in the equilibrium aqueous phase was assayed spectrophotometrically with Arsenazo III [18] and subsequently computed by the corresponding calibration graphs. The metal concentration in the equilibrium organic phase was then calculated as the difference between the metal content in the initial and the equilibrium aqueous phases. The acidity of the aqueous phase was measured with a pH meter with an accuracy of 0.01 pH unit.

RESULTS AND DISCUSSION

The investigation of the solvent extraction of the lanthanoid(III) metals with a ternary mixture of HP, HTTA and QCl requires an examination of the metal extraction with the individual extractants and with their binary mixtures as well.

The solvent extraction of the lanthanoid(III) metals with HP [19], HTTA [20], HTTA-QCl [21] and HP-QCl [22] has been studied previously. It has been found that the metal extraction can be represented by the following equations

$$Ln^{3+}_{(aq)} + 4HP_{(o)} \rightleftharpoons LnP_3.HP_{(o)} + 3H^+_{(aq)} \quad (1)$$

$$Ln^{3+}_{(aq)} + 3HTTA_{(o)} \rightleftharpoons Ln(TTA)_{3(o)} + 3H^+_{(aq)} \quad (2)$$

$$Ln^{3+}_{(aq)} + 4HP_{(o)} + QCl_{(o)} \rightleftharpoons Q[LnP_4]_{(o)} + 4H^+_{(aq)} + Cl^-_{(aq)} \quad (3)$$

$$Ln^{3+}_{(aq)} + 4HTTA_{(o)} + QCl_{(o))} \rightleftharpoons Q[Ln(TTA)_4]_{(o)} + 4H^+_{(aq)} + Cl^-_{(aq)} \quad (4)$$

where Ln^{3+} denotes a lanthanide ion and the subscripts "aq" and "o" denote aqueous and organic phases, respectively.

The values of the equilibrium constants K_P, K_T, $K_{P,Q}$ and $K_{T,Q}$ have also been calculated. The experimental data showed that the metal extraction with the quaternary ammonium salt QCl alone is negligibly small under the experimental conditions of the studies.

Thus, the metal extraction can be expressed by the equation:

$$Ln^{3+}_{(aq)} + 3HP_{(o)} + HTTA_{(o)} \rightleftharpoons LnP_3.HTTA_{(o)} + 3H^+_{(aq)} \quad (5)$$

The values of the overall equilibrium constant $K_{P,T}$ can be determined as:

$$\log K_{P,T} = \log D_{P,T} - 3\log[HP] - \log[HTTA] - 3\ pH \quad (6)$$

the formation of mixed adducts in the organic phase can be expressed:

$$LnP_3.HP_{(o)} + HTTA_{(o)} \rightleftharpoons LnP_3.HTTA_{(o)} + HP_{(o)} \quad (7)$$

The values of the constant $\beta_{P,T}$ can be determined by the equation:

$$\log \beta_{P,T} = \log K_{P,T} - \log K_P \quad (8)$$

The values of $\log K_{P,T}$ and $\beta_{P,T}$ are given in Table 1. The values of K_P [19] and K_T [20] are listed in the

Table 1. Values of the equilibrium constants K_P [19], K_T [20], $K_{P,T}$, $\beta_{P,T}$, $K_{P,T,Q}$ and $\beta_{P,T,Q}$ for the lanthanoid(III) ions extraction.

Ln^{3+}	$\log K_P$ [19]	$\log K_T$ [20]	$\log K_{P,T}$	$\log\beta_{P,T}$	$\log K_{P,T,Q}$	$\log\beta_{P,T,Q}$
La	-5.26	-10.51	-4.56	0.70	-0.50	4.06
Ce	-4.35	-9.43	-4.02	0.33	-0.25	3.77
Pr	-4.08	-8.85	-3.65	0.43	0.07	3.72
Nd	-3.50	-8.57	-3.16	0.34	0.27	3.43
Sm	-3.12	-7.68	-2.73	0.39	0.53	3.26
Eu	-2.99	-7.66	-2.69	0.30		
Gd	-3.04	-7.57	-2.57	0.47		

Error limits in the range $\leq \pm 0.05$.

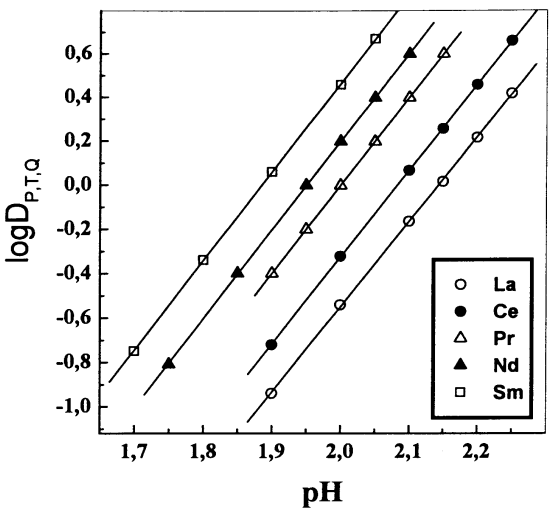

Fig. 1. Log $D_{P,T,Q}$ vs. pH for the extraction of lanthanoid elements with HP – HTTA – QCl mixture at [HP] = $2x10^{-2}$ mol dm^{-3}, [HTTA] =$2x10^{-2}$ mol dm^{-3} and [QCl] = $5x10^{-3}$ mol dm^{-3}.

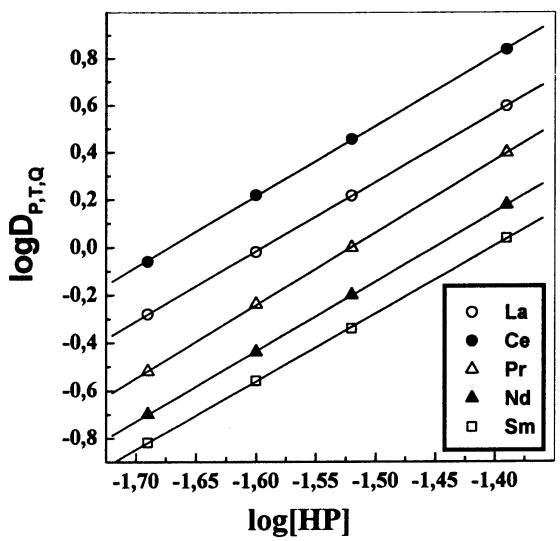

Fig. 2. Log $D_{P,T,Q}$ vs. log[HP] for the extraction of lanthanoid elements with HP – HTTA – QCl mixture at [HTTA]=$2x10^{-2}$ mol dm^{-3} and [QCl] =$5x10^{-3}$ mol dm^{-3}. La, pH=2.07; Ce, pH=2.07; Pr, pH = 1.87; Nd, pH=1.78; Sm, pH=1.68.

Table too. The equilibrium constants are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions. So they are concentration constants.

In the presence of three extractants (HP, HTTA and QCl) the experimentally obtained value of the distribution coefficient D_1 of a particular lanthanoid(III) metal is composed by several constituents: D_P, D_T (due to the extraction with HP and HTTA alone), $D_{P,T}$, $D_{P,Q}$ and $D_{T,Q}$ (due to the extraction with the binary mixtures HP – HTTA, HP – QCl and HTTA – QCl) and $D_{P,T,Q}$ (due to the extraction with the ternary mixture HP – HTTA – QCl). Therefore, the values of $D_{P,T,Q}$ can be calculated as:

$$D_{P,T,Q} = D_1 - D_P - D_T - D_{P,T} - D_{P,Q} - D_{T,Q} \quad (9)$$

The values of the distribution coefficients are given in Table 2. It is seen that most of them (D_P, D_T,

Table 2. Values of the distribution coefficients for the extraction of lanthanoid(III) ions with HP (D_P), HTTA (D_T), binary mixtures HP – HTTA ($D_{P,T}$), HP – QCl ($D_{P,Q}$), HTTA – QCl ($D_{T,Q}$) and a ternary mixture HP – HTTA – QCl ($D_{P,T,Q}$) at [HP] =2x10^{-2} mol dm^{-3}, [HTTA] = 2x10^{-2} mol dm^{-3}, [QCl] = 5x10^{-3} mol dm^{-3} and pH = 2.20 (D_1 is experimentally obtained distribution coefficient for the extraction with HP – HTTA - QCl mixture).

Ln^{3+}	D_1	D_P	D_T	$D_{P,T}$	$D_{P,Q}$	$D_{T,Q}$	$D_{P,T,Q}$
La	0.37	>10^{-6}	>10^{-9}	>10^{-5}	0.09	>10^{-5}	0.28
Ce	1.10	>10^{-5}	>10^{-8}	~10^{-5}	0.63	>10^{-4}	0.47
Pr	2.90	~ 10^{-5}	~10^{-8}	>10^{-4}	1.90	~10^{-4}	1.00
Nd	4.81	>10^{-4}	>10^{-7}	~10^{-4}	3.23	>10^{-3}	1.58
Sm	19.10	>10^{-4}	>10^{-6}	~10^{-4}	16.20	~10^{-3}	2.90
Eu	14.45	~10^{-4}	>10^{-6}	~10^{-4}	17.37	~10^{-3}	-
Gd	11.57	~10^{-4}	>10^{-6}	>10^{-3}	21.37	>10^{-2}	-

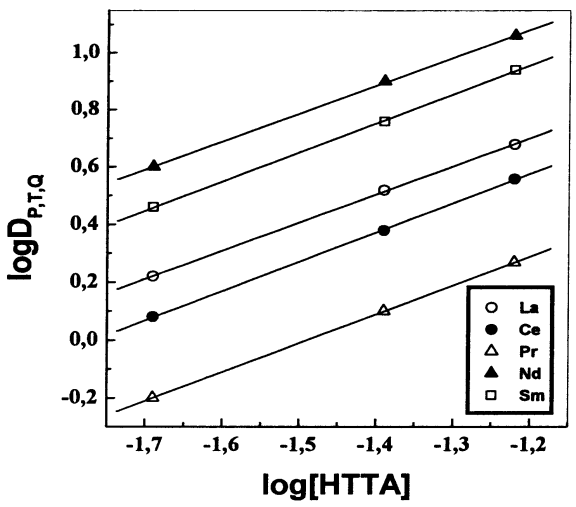

Fig. 3. Log $D_{P,T,Q}$ vs. log[HTTA] for the extraction of lanthanoid elements with HP – HTTA – QCl mixture at [HP] = 2x10^{-2} mol dm^{-3} and [QCl] = 5x10^{-3} mol dm^{-3}. La, pH=2.20; Ce, pH=2.10; Pr, pH=1.95; Nd, pH=2.10; Sm, pH=2.00.

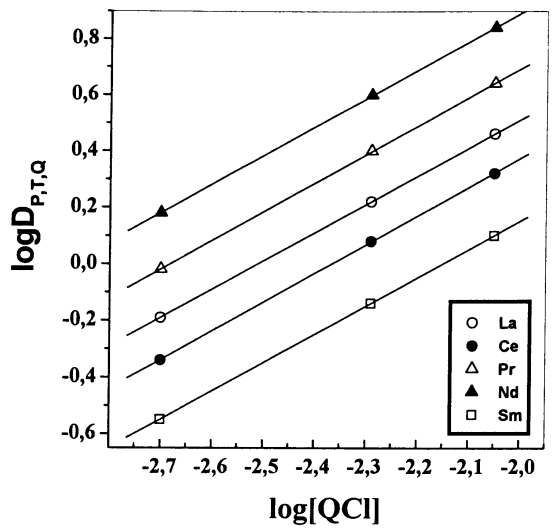

Fig. 4. Log$D_{P,T,Q}$ vs. log[QCl] for the extraction of lanthanoid elements with HP – HTTA – QCl mixture at [HP] = 2x10^{-2} mol dm^{-3} and [HTTA] =2x10^{-2} mol dm^{-3}. La, pH=2.20; Ce, pH=2.10; Pr, pH=2.10; Nd, pH=2.10; Sm, pH=1.85.

$D_{P,T}$ and $D_{T,Q}$) are negligibly small under the experimental conditions. Thus the values of $D_{P,T,Q}$ were calculated as D_1 - $D_{P,Q}$.

The stoichiometry of the synergistic complex was studied by examination of the plots of log $D_{P,T,Q}$ vs. pH, log[HP], log[HTTA] and log[QCl]. These plots are linear with slopes close to 4, 3, 1 and 1 (Figs. 1-4).

Therefore, the synergistic extraction with the ternary mixture can be described as follows:

$$Ln^{3+}_{(aq)} + 3HP_{(o)} + HTTA_{(o)} + QCl_{(o)} \rightleftharpoons Q[LnP_3(TTA)]_{(o)} + 4H^+_{(aq)} + Cl^-_{(aq)} \quad (10)$$

where Ln^{3+} denotes La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}.

The overall equilibrium constant $K_{P,T,Q}$ can be determined as:

$$\log K_{P,T,Q} = \log D_{P,T,Q} + \log[Cl^{1}] - 4pH - 3\log[HP] - \log[HTTA] - \log[QCl] \quad (11)$$

The organic phase synergistic reaction can be expressed by the equation:

$$LnP_3.HTTA_{(o)} + QCl_{(o)} \rightleftharpoons Q[LnP_3(TTA)]_{(o)} + H^+_{(aq)} + Cl^-_{(aq)} \quad (12)$$

The equilibrium constant $\beta_{P,T,Q}$ can be calculated as:

$$\log b_{P,T,Q} = \log K_{P,T,Q} - \log K_{P,T} \quad (13)$$

The values of the equilibrium constants $K_{P,T,Q}$ and $\beta_{P,T,Q}$ are listed in Table 1. The values of $K_{P,T,Q}$ increase from La to Sm but those of $\beta_{P,T,Q}$ decrease in that order.

The data in Table 2 show that the value of $D_{P,T,Q}$ is larger than $D_{P,Q}$ for La but for Ce, Pr, Nd and Sm the trend is reversed i.e. the values of $D_{P,Q}$ become larger. Surprisingly, for Eu and Gd the values of $D_{P,Q}$ are even larger than those of D_1. Hence, synergistic effect is observed for La, Ce, Pr, Nd and Sm but antagonistic effect is established for Eu and Gd. A plausible explanation of this fact is not yet found as formation of the complexes $Q[LnP_4]$ [22] and $Q[Ln(TTA)_4]$ [21] was established for the entire lanthanoid series.

CONCLUSIONS

In the presence of a ternary mixture of extractants (HP, HTTA and QCl) extraction of an anionic complex $Q[LnP_3(TTA)]$ was established. Synergistic effect was observed for La, Ce, Pr, Nd and Sm but antagonistic effect was found for Eu and Gd.

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REFERENCES

1. Y. Marcus, A. S Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, Wiley Intercience, New York, 1969.
2. T. V. Healy, Synergistic Adducts as Coordination Compounds. Proc. Fifth Int. Conf. on Solvent Extr. Chem., Jerusalem, Israel, 16-18 Sept. 1968, pp. 257-279.
3. G. Duyckaerts, J. F Desreux, in: B. H. Lucas, G. M. Ritcey, H. M. Smith, (Eds.) Int. Solv. Extr. Conf. (ISEC'77), Toronto, Sept. 9 – 16, 1977, CIM Special vol. 21, 1979, pp. 73-85.
4. J. Hala, J. Radioanal. Chem. **51**, 1979, 15-25.
5. J. N. Mathur, Solvent Extr. Ion Exch. **1**, 1983, 349-412.
6. J. Chen, L. Zhang, New Frontiers of Rare Earths Sci. and Appl. Proc. Int. Int. Conf., Beijing, China, Sept. 10-14, 1985, vol. 1, pp. 499-502.
7. J. Chen, H. Zhao, Zhongguo Xitu Xuebao, **11**, 1993, 97-100 (CA 120:308597).
8. W. Wang, M. Yi, D.Chen, in: Int. Solvent Extr. Conf. (ISEC'83), Denver, COLO, 26 Aug. – 2 Sept., 1983, pp. 483 – 484.
9. J. Chen, W. Wang, He Huaxue Yu Fangshe Huaxue **15**, 1993, 50-55 (CA: 120:281614).
10. J. Du,Yigyong Huaxue **12**, 1995, 58-61 (CA 124: 99120).
11. Du, J. He Huaxue Yu Fangshe Huaxue **17**, 1995, 230-236 (CA 124: 326293).
12. W. Wang, Y. Ding, Youkiangue **11**, 1992, 41-46 (CA 120: 281624).
13. H. Irving in: M. Beck (Ed.), The Solvent Extraction of Mixed Complexes. Proc. Symp. Coord. Chem., Tihany, Hungary Acad. Kiado, Budapest, 1965, pp. 219-228.
14. I. Dukov, L.Genov, J. Inorg. Nucl. Chem. **43**, 1981, 412-413.
15. W. D'Olieslager, L.Sanen, M. De Jong, J. Less - Common Met. **112**, 1985, 235-242.
16. T. Sekine, D. Dyrssen, J. Inorg. Nucl. Chem. **29**, 1967, 1489-1498.
17. T. Goto, J. Inorg. Nucl. Chem. **31**, 1969, 1111-1119.
18. S. B. Savvin, Arsenazo III, Atomizdat, Moskva, 1966, p. 177 (in Russian).
19. V. Jordanov, M. Atanassova, I. Dukov, Sep. Sci. Technol. **37**, 2002, 3349-3356.

20. A. M. Poskanzer, B. M. A. Foreman, J. Inorg. Nucl. Chem. **2**, 1961, 323-336.
21. M. Atanassova, V. M. Jordanov, I. L. Dukov, Hydrometallurgy **63**, 2002, 41-47.
22. I. L. Dukov, M. Atanassova, Separ. Sci. Technol. **39** (1), 2004, 227-239.