

Solvent extraction and separation of lanthanoids with mixtures of chelating extractant and 1-(2-pyridylazo)-2-naphthol

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Abstract

The solvent extraction of trivalent lanthanoids (without Pm) with mixtures of chelating extractant 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (thenoyltrifluoroacetone, HTTA) or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-on (HP) and 1-(2-pyridylazo)-2-naphthol (PAN, S) in C_6H_6 has been studied. It was found that in the presence of 1-(2-pyridylazo)-2-naphthol the lanthanoids have been extracted as $Ln(TTA)_3S$ and LnP_3S . On the basis of the experimental data, the values of the equilibrium constants have been calculated. The addition of PAN to the chelating extractant produces synergistic effect which is larger for the heavier lanthanoids. The separation of the lanthanoids with synergistic mixtures was higher than those obtained with HTTA or HP alone. In the most cases an enhancement of the metal ions separation was observed upon the change of the chelating extractant HP with HTTA.

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Keywords: Lanthanoids; Synergistic extraction; 1-(2-Thienyl)-4,4,4-trifluoro-1,3-butanedione; 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-on; 1-(2-Pyridylazo)-2-naphthol; Separation factors

1. Introduction

Solvent extraction has been widely employed as a versatile separation method of metal ions in various fields from analytical chemistry to hydrometallurgy because of its simplicity, speed, and applicability to both tracer and macroamounts 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 extraction of trivalent actinoids and lanthanoids is of great interest because of the high extraction efficiency of these metal ions in presence of a chelating agent and a neutral donor [1–7]. The separation of the lanthanoids and actinoids has also been discussed [8–12]. Thenoyltrifluoroacetone and a large number of 4-acyl-5-pyrazolones have been extensively used as extractants for lanthanoids and other elements separately and in combination with various synergistic agents [2–4,13–16].

1-(2-Pyridylazo)-2-naphthol (further abbreviated as PAN or S) has been used several times for the extraction of metals [13,17,18].

The object of the present work is to investigate the synergistic solvent extraction of the metals of the lanthanoid series with mixture of a chelating extractant 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (HTTA) or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-on (HP) and 1-(2-pyridylazo)-2-naphthol (PAN) in C_6H_6 and to determine the possibilities for the separation of the metals.

2. Experimental

2.1. Reagents

The commercial products HTTA (purity >99%, Fluka), HP (purity >99%, Fluka) and PAN (p.a., Fluka) were used as received. The diluent was benzene (Merck, p.a.). Stock solutions of the metals were prepared from their oxides (Fluka, puriss.). Arsenazo III (Fluka) was of analytical grade purity as were the other reagents used.

2.2. 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

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to reach equilibrium. After the separation of the phases, the metal concentration in the aqueous phase was determined photometrically using Arsenazo III [19]. 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/dm³ with (Na, H)Cl. The initial concentration of the metals was 2.5×10^{-4} mol/dm³ in all experiments.

The distribution coefficients of the lanthanoids were determined in three series of experiments:

- with fixed HTTA(HP) and PAN concentration and varied pH;
- with fixed pH and PAN concentration and varied HTTA(HP) concentration;
- with fixed pH and HTTA(HP) and varied PAN concentration.

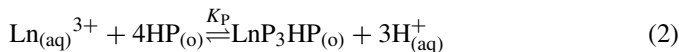
3. Results and discussion

The solvent extraction of the lanthanoid(III) ions with HTTA in C₆H₆ has been studied previously by Poskanzer and Foreman [15]. It has been found that the metal extraction can be represented by the following equation:



where Ln³⁺ denotes a lanthanoid ion and the subscripts “aq” and “o” denote aqueous and organic phases, respectively.

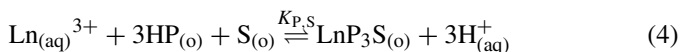
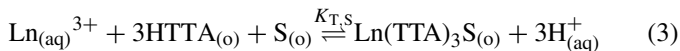
The solvent extraction of 13 lanthanoid metals with HP alone in C₆H₆ has been studied by Dukov et al. [20]. The extraction process can be described by the equation:



The synergistic solvent extraction of the lanthanoids was studied using a traditional and effective means of obtaining both stoichiometric and equilibrium constant information about extraction processes, called “slope analysis”. It is based on an examination of the variation of $D_{T,S}$ or $D_{P,S}$ (the distribution coefficient due to the synergistic effect) as a function of the relevant experimental variables. As the lanthanoids extraction with PAN alone is negligible under the experimental conditions of the present study, the values of the distribution coefficient D obtained experimentally are the sum of $D_{T,S}$ and D_T or $D_{P,S}$

and D_P (D_T and D_P are the distribution coefficients due to the lanthanoid extraction with HTTA or HP alone under the same experimental conditions). So, the values of $D_{T,S}$ ($D_{P,S}$) were calculated as $D - D_T$ (D_P). A log–log plot of $D_{T,S}$ ($D_{P,S}$) versus one of the variables [H⁺], [HTTA(HP)] and [PAN, S] keeping the other two constant, indicates the stoichiometry of the extractable complex, and thus leads 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 the hydrolysis in the aqueous phase as well as the 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 of the adducts.

The experimental data for the extraction of the lanthanoid metals with mixture of HTTA–PAN and HP–PAN are given in Figs. 1–6. The plots of log $D_{T,S}$ ($D_{P,S}$) versus pH and log[HTTA (HP)] are linear with slope close to three and the plots of log $D_{T,S}$ ($D_{P,S}$) versus log[S] with slope close to one. Therefore, in the presence of HTTA–PAN and HP–PAN the lanthanoid extraction can be expressed by the following equations:



The formation of the species Ln(TTA)₃S or LnP₃S is in accordance with the statement of Marcus and Kertes [22, p. 853] that a combination of one weak and one strong β-diketone can produce extraction of a mixed adduct accompanied by a synergistic effect as well as with the statement of Hala [23] that the weaker acid is involved in the mixed adduct as a neutral molecule (the pK_a values of HTTA, HP and PAN are 6.2 [15], 3.95 [14] and 11.2 [21], respectively).

Taking into account that the partition of HP [14], HTTA [15] and PAN [21] toward the aqueous phase is very low and on the basis of the slope analysis data, the overall equilibrium constants $K_{T,S}$ and $K_{P,S}$ can be determined by the equations:

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

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

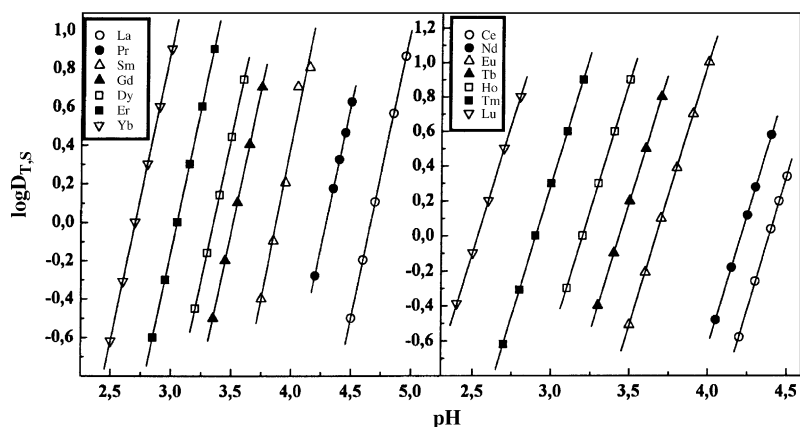


Fig. 1. log $D_{T,S}$ vs. pH for the extraction of lanthanoid elements with HTTA–PAN mixture at [HTTA] = 3×10^{-2} mol/dm³ and [PAN] = 5×10^{-3} mol/dm³.

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