SYNERGISTIC SOLVENT EXTRACTION OF TRIVALENT LANTHANIDES BY MIXTURES OF 1-PHENYL-3-METHYL-4-TRIFLUOROACETYL-PYRAZOLONE-5 AND NEUTRAL OXO-DONORS

S. SUJATHA, M.L.P. REDDY*, R. LUXMI VARMA, T.R. RAMAMOCHAN, T. PRASADA RAO, C.S.P. IYER AND A.D. DAMODARAN

Regional Research Laboratory (CSIR), Trivandrum-695 019, India

Key words: Solvent Extraction, Lanthanides, 4-Acyl Pyrazolone, Neutral Oxo-Donors, Separation Factors

Introduction

Acyl pyrazolones in general and 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) in particular, are efficient ligands for the extraction of trivalent lanthanides

and actinides. Such metal ions are extractable from acid media because of the strong acidity of the pyrazolone ($pK_a = 2.5$ to 4.0). Among 4-acyl pyrazolones, 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP) exhibits an extremely strong acidity ($pK_a = 2.56$) caused by the strong electron withdrawing nature of the trifluoromethyl group. Umetani and Fresier (1987) have studied the

* Received on August 17, 1995.

** Correspondence concerning this article should be addressed to M.L. P. Reddy.

mixed-ligand chelate extraction of lanthanides with HPMTFP and tri-octylphosphine oxide or octyl (phenyl)-N, N-diisobutyl carbamoyl methyl phosphine oxide (CMPO). However, systematic studies of synergistic solvent extraction systems involving dialkyl sulphoxide as a neutral donor in the presence of HPMTFP are sparse.

Bis-2-ethylhexyl sulphoxide (B2EHSO), a novel sterically hindered branched chain extractant has been recently explored as a synergist for the extraction of trivalent lanthanides and actinides in the presence of thenoyltrifluoroacetone (HTTA), HPMBP and 1-phenyl-3-methyl-4-acetyl-pyrazolone-5 (HPMAP) in our laboratory (Santhi *et al.*, 1994b; Santhi *et al.*, 1994c; Sujatha *et al.*, 1994). The addition of B2EHSO to the metal chelate system improves the separation factors between trivalent lanthanides. This gives added impetus to further investigate new synergistic solvent extraction systems. In this paper, we report the synergistic solvent extraction of trivalent lanthanides and actinides with mixtures of HPMTFP and B2EHSO or triphenylphosphine oxide (TPhPO) in chloroform with a view to elucidate the nature of the species extracted into the organic phase and to investigate the selectivity of these mixed-ligand systems.

1. Experimental

1-Phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP) was synthesised in our laboratory by the procedure described by Jensen (1959). Bis-2-ethylhexyl sulphoxide (B2EHSO) was purchased from Fairfield Chemical Co., USA, and purified by the method reported in the literature (Santhi *et al.*, 1994a). Triphenylphosphine oxide (TPhPO) was obtained from Aldrich Chemical Co., The radioactive tracers ^{147}Nd , $^{152,154}\text{Eu}$ and ^{177}Lu were supplied by Board of Radiation and Isotope Technology (BRIT), India.

Stock solutions of lanthanides were prepared from their oxides (Rare Earth Products, Cheshire, U.K., 99.99%) by dissolving in concentrated hydrochloric acid and diluting with distilled water. Initial metal ion concentration was maintained at 1×10^{-6} mol/dm³. The experimental details and the solvent extraction procedure followed in this paper was described in our previous publications (Sujatha *et al.*, 1994. Santhi *et al.*, 1994b).

2. Results and Discussion

2.1 Extraction of trivalent lanthanides with HPMTFP alone

The lanthanide ion in the aqueous phase takes a variety of complex forms in the presence of chloroacetate ions, however under the present experimental conditions, it will form only the first two complexes defined by

where $\text{Ln}^{3+} = \text{Nd, Eu and Lu}$, $\text{Cl} \cdot \text{Ac}^- =$ the chloroac-

Table 1. Two-phase equilibrium constants of trivalent lanthanides with HPMTFP-neutral oxo-donor systems

Complex	Nd(III)	Equilibrium constant	
		Eu(III)	Lu(III)
$\text{Lu}(\text{PMTFP})_3$	1.98×10^{-4}	1.11×10^{-3}	2.74×10^{-3} [-]
$\text{Ln}(\text{PMTFP})_3 \cdot \text{B2EHSO}$	3.42×10^{-1}	0.2×10^{-1}	1.34×10^1 [(mol/dm ³) ⁻¹]
$\text{Ln}(\text{PMTFP})_3 \cdot 2\text{B2EHSO}$	1.77×10^1	1.99×10^2	2.78×10^2 [(mol/dm ³) ⁻²]
$\text{Ln}(\text{PMTFP})_3 \cdot \text{TPhPO}$	1.49×10^1	1.5×10^2	4.7×10^2 [(mol/dm ³) ⁻¹]
$\text{Ln}(\text{PMTFP})_3 \cdot 2\text{TPhPO}$	9.30×10^1	5.47×10^5	2.7×10^6 [(mol/dm ³) ⁻²]

etate ion and $i = 1, 2$. Then the total Ln (III) concentration in the aqueous phase (Ln_i) is given by

$$\text{Ln}_i = [\text{Ln}^{3+}] \{1 + \beta_1 [\text{Cl} \cdot \text{Ac}] + \beta_2 [\text{Cl} \cdot \text{Ac}]^2\} \quad (2)$$

The values of the stability constants were obtained from the literature (Smith and Martell, 1976). Chloroacetate ion concentration was calculated with the knowledge of dissociation equilibrium of chloroacetic acid ($\text{HA} \xrightleftharpoons{K_a} \text{H}^+ + \text{A}^-$; $\text{pK}_a = 2.85$) and material balances ($\text{HA}_{\text{Total}} = \text{HA} + \text{A}^-$).

The extraction equilibria of Nd (III), Eu (III) and Lu (III) with HPMTFP alone may be expressed as

The distribution coefficient, D , is given by

$$D = \frac{K_{\text{PMTFP}} [\text{HPMTFP}]^3}{[\text{H}^+]^3 (1 + \beta_1 [\text{Cl} \cdot \text{Ac}] + \beta_2 [\text{Cl} \cdot \text{Ac}]^2)} \quad (4)$$

where bars denote the organic phase.

The extraction of trivalent lanthanides Nd, Eu and Lu from 0.01 mol/dm³ chloroacetate buffer solution with HPMTFP alone in chloroform as a function of extractant concentration (0.005-0.08 mol/dm³ HPMTFP) and pH (2.2 to 2.7), respectively was studied. The relevant log-log plots give straight lines with slopes of 3, indicating that the extraction of the simple metal chelates, $\overline{\text{Ln} (\text{PMTFP})_3}$. The extraction constants for the above species were determined by non-linear regression analysis (Santhi *et al.*, 1991) and are shown in **Table 1**. It can be clearly seen from Table 1 that the equilibrium constants (K_{PMTFP}) of these trivalent metal ions increase with decreasing ionic radii of the Ln^{3+} ion. Comparing the equilibrium constants of various β -diketones for the extraction of Eu (III) ($K_{\text{TTA}} = 1.48 \times 10^{-7}$ (Santhi *et al.*, 1994c); $K_{\text{PMAP}} = 1.70 \times 10^{-5}$ (Sujatha *et al.*, 1994); $K_{\text{PMTFP}} = 1.11 \times 10^{-3}$ (present values) with their pK_a values (HTTA = 6.25; HPMA = 3.78; HPMTFP = 2.56), it can be concluded that the equilibrium constant values increase as pK_a decreases.

2.2 Extraction of trivalent lanthanides with a mixture of HPMTFP and B2EHSO or TPhPO

The extraction equilibria of Nd (III), Eu(III) and Lu(III) with HPMTFP in the presence of a synergist (S) can be written as

Fig. 1 Effect of B2EHSO concentration on the extraction of trivalent lanthanides Nd, Eu and Lu at fixed HPMTFP concentration. Aqueous phase: 0.01 mol/dm³ chloroacetate buffer solution of pH=2.7

where n = the number of auxiliary reagent molecules attached to the chelate system and is equal to 1 or 2.

Then D can be written as

$$D = \sum_{n=0}^2 \frac{K_{\text{syn},n} [\text{PMTFP}]^3 [\text{S}]^n}{[\text{H}^+]^3 (1 + \beta_1 [\text{Cl} \cdot \text{Ac}] + \beta_2 [\text{Cl} \cdot \text{Ac}]^2)} \quad (6)$$

It should be noted that there is negligible interaction between HPMTFP and neutral oxo-donors in chloroform as a diluent as was confirmed experimentally. Sekine *et al.* (1983) also stated that the interactions between a β -diketone and a neutral oxo-donor, TOPO in chloroform, is in general, weaker when the solvent-solute interactions is stronger.

The adduct formation reaction in the organic phase and the stability constant, β_n , is given by

$\beta_n = K_{\text{syn},n} / K_{\text{PMTFP}}$, where $n = 1$ or 2. K_2 is defined as the equilibrium constant for the reaction

and can be calculated as

$$K_2 = \beta_2 / \beta_1 \quad (9)$$

The extraction of trivalent Nd, Eu and Lu from 0.01 mol/dm³ chloroacetate buffer solution of pH = 2.7 with mixtures of HPMTFP (0.006-0.04 mol/dm³) and B2EHSO (0.002-0.02 mol/dm³) in chloroform was studied. It was found that these metal ions are not extracted in practice by B2EHSO alone into chloroform from chloroacetate solutions at pH = 2.7. However, with mixtures of (HPMTFP + B2EHSO), about 10-fold to 100-fold enhancement in the extraction of these metal ions has been observed. It is clear from the plot of $\log \{ D [\text{H}^+]^3 (1 + \beta_1 [\text{Cl} \cdot \text{Ac}] + \beta_2 [\text{Cl} \cdot \text{Ac}]^2) / (1 + \frac{K_{\text{syn},1}}{K_{\text{PMTFP}}} [\text{B2EHSO}] + \frac{K_{\text{syn},2}}{K_{\text{PMTFP}}} [\text{B2EHSO}]^2) \}$ (rearrangement of Eq.

Fig. 2 Effect of TPhPO concentration on the extraction of trivalent lanthanides Nd, Eu and Lu at fixed HPMTFP concentration. Aqueous phase: 0.01 mol/dm³ chloroacetate buffer solution of pH=2.7

(6)) versus $\log [\text{HPMTFP}]$ that at constant B2EHSO only three HPMTFP moieties are attached to the synergistic species in all the systems studied here.

The plots (Fig. 1) of $\log \{ D [\text{H}^+]^3 (1 + \beta_1 [\text{Cl} \cdot \text{Ac}] + \beta_2 [\text{Cl} \cdot \text{Ac}]^2) / ([\text{HPMTFP}]^3 - K_{\text{PMTFP}}) \}$ (rearrangement of Eq. (6)) versus $\log [\text{B2EHSO}]$ at constant HPMTFP concentration yields a slope of non-interger value between 1 and 2. These, in conjunction with the slope of 3 observed with pH variation (pH = 2.2 to 2.7 at constant 0.01 mol/dm³ HPMTFP + 0.01 mol/dm³ B2EHSO concentration) indicates the extraction of the species, $\text{Ln}(\text{PMTFP})_3 \cdot \text{B2EHSO}$ and $\text{Ln}(\text{PMTFP})_3 \cdot 2\text{B2EHSO}$. This was further confirmed by analysing the equilibrium data using Eq. (6). The synergistic extraction constants for the species ($K_{\text{syn},1}$ and $K_{\text{syn},2}$) were obtained by nonlinear regression analysis and are shown in Table 1.

The extraction of trivalent Nd, Eu and Lu from 0.01 mol/dm³ chloroacetate buffer solution of pH = 2.7 with mixtures of HPMTFP (0.004-0.04 mol/dm³) and TPhPO (0.00002-0.0001 mol/dm³) in chloroform was also investigated. It was found that the extraction of these metal ions is negligible with TPhPO alone under the experimental conditions. About 10-fold to 50-fold enhancement in the extraction of these metal ions has been observed in these systems. The plots of $\log \{ D [\text{H}^+]^3 (1 + \beta_1 [\text{Cl} \cdot \text{Ac}] + \beta_2 [\text{Cl} \cdot \text{Ac}]^2) / (1 + \frac{K_{\text{syn},1}}{K_{\text{PMTFP}}} [\text{TPhPO}] + \frac{K_{\text{syn},2}}{K_{\text{PMTFP}}} [\text{TPhPO}]^2) \}$ versus $\log [\text{HPMTFP}]$ at constant TPhPO concentration are linear with slopes equal to 3 ± 0.02 for all the metal ions, indicating that 3 molecules of HPMTFP are involved in the respective extractable complexes. It can be clearly seen from Fig. 2 ($\log \{ D [\text{H}^+]^3 (1 + \beta_1 [\text{Cl} \cdot \text{Ac}] + \beta_2 [\text{Cl} \cdot \text{Ac}]^2) / ([\text{HPMTFP}]^3 - K_{\text{PMTFP}}) \}$ versus $\log [\text{TPhPO}]$) that the slopes of the plots vary between 1 and 2. These, in conjunction with the slope of 3 observed with pH variation (pH = 2.2 to 2.7 at constant 0.01 mol/dm³ HPMTFP + 0.00002 mol/dm³ TPhPO

Table 2. Equilibrium constants for the organic phase synergistic reactions of trivalent lanthanide-HPMTFP chelates with B2EHSO or TPhPO

Ln(III)	$\beta_1[(\text{mol}/\text{dm}^3)^{-1}]$	$\beta_2[(\text{mol}/\text{dm}^3)^{-2}]$	$K_2[(\text{mol}/\text{dm}^3)^{-1}]$
HPMTFP+B2EHSO			
Nd	3.17×10^3	1.64×10^5	5.17×10^1
Eu	1.98×10^3	1.71×10^5	8.63×10^1
Lu	4.89×10^3	1.01×10^5	2.06×10^1
HPMTFP+TPhPO			
Nd	1.38×10^5	8.60×10^5	0.62×10^1
Eu	1.36×10^5	4.93×10^8	3.62×10^3
Lu	1.72×10^5	1.0×10^9	5.81×10^3

Table 3. Separation factors for trivalent lanthanides with (HPMTFP+B2EHSO) systems

Extraction system	Separation factors	
	Eu/Nd	Lu/Eu
(0.01 mol/dm ³ HPMTFP)	10.9	2.7
(0.1 mol/dm ³ HPMTFP+ (0.005 mol/dm ³ B2EHSO)	7.8	5.1
(0.01 mol/dm ³ HPMTFP+ 0.0001 mol/dm ³ TPhPO	14.4	4.0

concentration) for all these metal ions; indicates the extraction of the species, $\text{Ln}(\text{PMTFP})_3 \cdot \text{TPhPO}$ and $\text{Ln}(\text{PMTFP})_3 \cdot 2\text{TPhPO}$. The equilibrium constants of the species are shown in Table 1.

It can be clearly seen from Table 1 that the synergistic extraction constants ($K_{\text{syn}, 1}$ and $K_{\text{syn}, 2}$) for both systems studied here increases with decreasing ionic radii of these metal ions. The stability constants β_1 , β_2 and k_2 for trivalent lanthanides calculated according to Eqs. (7) and (9) are given in Table 2. The adduct formation constant of Eu-HPMTFP-B2EHSO ($\beta_2 = 1.7 \times 10^5$) is higher than that of Eu-HTTA-B2EHSO (Santhi *et al.*, 1994c) system ($\beta_2 = 7.7 \times 10^4$) and Eu-HPMAP-B2EHSO (Sujatha *et al.*, 1994) system ($\beta_2 = 1.12 \times 10^4$). It is well known that stable adduct formation reactions are usually brought about by strong acidic extractants as observed in the present systems.

Table 3 gives the separation factors (S.F.) between these trivalent lanthanides defined as the ratio of the respective distribution coefficients with 0.01 mol/dm³ HPMTFP, (HPMTFP 0.01 mol/dm³ + 0.005 mol/dm³ B2EHSO) and (HPMTFP 0.01 mol/dm³ + TPhPO 0.0001 mol/dm³) systems. It is interesting to note that the addition of B2EHSO or TPhPO to the chelate system improves the S.F. values between the Lu-Eu pair. In the case of the Eu-Nd pair, the S.F. values with mixtures of (HPMTFP + B2EHSO) decreases but it increases moderately with mixtures of HPMTFP and TPhPO.

Conclusion

The extraction equilibria of trivalent lanthanides with HPMTFP and also with mixtures of (HPMTFP + B2EHSO or TPhPO) has been investigated. The results demonstrate that not only enhanced extraction but also improved separation factors among these trivalent lanthanides can be achieved with mixed-ligand systems. Hence, such a system would be of practical value in the extraction and separation of these metal ions.

Nomenclature

D	=	distribution coefficient	[-]
K_{PMTFP}	=	extraction constant of the complex defined by Eq. (3)	[-]
$K_{\text{syn}, 1}$ ($n = 1, 2$)	=	extraction constant of the reaction defined by Eq. (5)	$[(\text{mol}/\text{dm}^3)^{-n}]$
K_2	=	equilibrium constant of the reaction defined by Eq. (9)	$[(\text{mol}/\text{dm}^3)^{-1}]$
β_n ($n = 1, 2$)	=	stability constant of the complex defined by Eq. (7)	$[(\text{mol}/\text{dm}^3)^{-n}]$
$\beta_{\text{h}, \text{Ln}}$ ($l = 1, 2$)	=	stability constant of the lanthanide chloroacetate complex	$[(\text{mol}/\text{dm}^3)^{-1}]$

Literature Cited

- Jensen, B.S.; "The Synthesis of 1-Phenyl-3-methyl-4-acyl-Pyrazolones-5," *Acta Chem. Scand.* **13**, 1668-1670 (1959).
- Santhi, P.B., M.L.P. Reddy, T.R. Ramamohan, and A.D. Damodaran; "Radiochemical Extraction of Lanthanide Thiocyanate Complexes with Bis-2-ethylhexyl Sulphoxide," *Radiochim. Acta*, **64**, 121-125 (1994a).
- Santhi, P.B., M.L.P. Reddy, T.R. Ramamohan, A.D. Damodaran, J.N. Mathur, M.S. Murali, and R.H. Iyer; "Synergistic Solvent Extraction of Trivalent Lanthanides and Actinides by Mixtures of 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 and Neutral Oxo-Donors," *Solvent Extr. Ion Exch.*, **12**, 633-650 (1994b).
- Santhi, P.B., M.L.P. Reddy, T.R. Ramamohan and A.D. Damodaran; "Mixed-Ligand Chelate Extraction of Lanthanides with Thenoyltrifluoroacetone and Bis-2-ethylhexyl Sulphoxide," *Radiochim. Acta*, **64**, 205-209 (1994c).
- Santhi, P.B., M.L.P. Reddy, T.R. Ramamohan, and A.D. Damodaran; "Liquid-Liquid Extraction of Yttrium (III) with Mixtures of Organophosphorus Extractants: Theoretical Analysis of Extraction Behavior," *Hydrometallurgy*, **27**, 169-177 (1991).
- Sekine, T., T. Saitou and H. Iga; "Association of B-Diketones with Triethylphosphine Oxide in Solvent Extraction Systems," *Bull. Chem. Soc. Japan*, **56**, 700-704 (1983).
- Smith, R.M. and A.E. Martell; *Critical Stability Constants*, vol.4, Plenum Press, New York (1976).
- Sujatha, S., M.L.P. Reddy, T.R. Ramamohan, A.D. Damodaran, J.N. Mathur, M.S. Murali, M.S. Nagar, and R.H. Iyer; "Solvent Extraction of Trivalent Lanthanides and Actinides by Mixtures of 1-Phenyl-3-methyl-4-acetyl-pyrazolone-5 and Neutral Oxo-donors," *Radiochim. Acta*, **65**, 167-172 (1994).
- Umetani, S., and H. Freiser; "Mixed-ligand Chelate Extraction of Lanthanides with 1-Phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone-5 and Some Phosphine Oxide Compounds," *Inorg. Chem.*, **26**, 3179-3181 (1987).