Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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I. L. Dukov[a]; V. M. Jordanov[a]
[a] DEPARTMENT OF INORGANIC CHEMISTRY, UNIVERSITY OF CHEMICAL TECHNOLOGY AND METALLURGY 8, SOFIA, BULGARIA

To cite this Article Dukov, I. L. and Jordanov, V. M.(1997) 'Synergism and Separation Factors in Lanthanide Extraction with Mixtures of Chelating Extractant and Amine Salts in C_6H_6', Separation Science and Technology, 32: 15, 2561 — 2568
To link to this Article: DOI: 10.1080/01496399708000786
URL: http://dx.doi.org/10.1080/01496399708000786

SEPARATION SCIENCE AND TECHNOLOGY, 32(15), pp. 2561–2568, 1997

TECHNICAL NOTE

Synergism and Separation Factors in Lanthanide Extraction with Mixtures of Chelating Extractant and Amine Salts in C_6H_6

I. L. DUKOV and V. M. JORDANOV
DEPARTMENT OF INORGANIC CHEMISTRY
UNIVERSITY OF CHEMICAL TECHNOLOGY AND METALLURGY
8, KLIMENT OCHRIDSKI BLVD., 1756 SOFIA, BULGARIA

ABSTRACT

The solvent extraction of Pr, Gd, and Yb with 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HP) and an amine salt (AmHA) has been studied. The composition of the extracted species has been determined as (AmH)[LnP_4]. The values of the synergistic coefficients and separation factors have been calculated. The effect of the amine salt on the extraction and separation of lanthanides has been discussed.

Key Words. Synergistic extraction; Lanthanides; 1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one; Aliphatic amines; Separation factors

INTRODUCTION

The synergistic solvent extraction of lanthanides has been extensively studied for a long time (1, 2). Mixtures of chelating extractants and organophosphorus compounds, high molecular weight amines, or quaternary ammonium salts have often been used. Large synergistic enhancements have been reported. However, the possibilities for lanthanide separation have been discussed only in a few investigations. Freiser et al. (3–7) studied the synergistic extraction of lanthanide ions and separation factors of the pairs Pr/La, Eu/Pr, and Yb/Eu using mixtures of acylpyrazolones and trioctylphosphine oxide, 1,10-phenanthroline, or methyltrioctylammonium chloride. Reddy et al. (9, 10) investigated the extraction and separation of La, Pr, Eu, and Am with benzoylpyrazolone (HP) and with mixtures of HP and bis(2-ethylhexyl) sulfoxide (B2EHSO) or octyl(phenyl)-*N*-*N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO). New extracting agents (3-phenyl-4-acyl-5-isoxalones) in combination with tributyl phosphate (TBP) or B2EHSO have shown an increase in the separation of Eu and Am (11), but the separation factors of the pairs Eu/Pr and Yb/Eu were small (12). Mixtures of thenoyltrifluoroacetone (HTTA) and 2,2-bipyridine (8) or monothiothenoyltrifluoroacetone (HSTTA) and crown ethers (13) have also been used for lanthanide extraction and separation. The influence of the factors affecting the selectivity of the synergistic extraction was discussed by Akaiwa (14).

In the present paper the effect of various amine salts on the synergism and separation in the extraction of representative tervalent lanthanides (Pr, Gd, and Yb) with HP was studied.

EXPERIMENTAL

Reagents

HP (Pharmachim Sofia, p.a.) and trioctylamine (TOA), methyldioctylamine (MDOA) and dioctylamine (DOA) (Fluka, purum) were used as supplied. The oxides Pr_6O_{11}, Gd_2O_3, and Yb_2O_3 (Fluka, puriss.) were used to prepare the stock solutions of the metals. Benzene (Merck, p.a.) was used as the diluent. The other reagents used were of analytical reagent grade.

Procedure

Equal volumes (10 cm^3 each) of the aqueous and organic phases were shaken mechanically for 60 minutes at room temperature, which was sufficient to reach equilibrium. After phase separation the metal concentration in the aqueous phase was determined photometrically using Arsenazo III (15). 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 (Na, H)Cl, ClO_4. The initial metal concentration was 2.5 $\times$ 10^{-4} mol/dm^3 in all experiments.

RESULTS AND DISCUSSION

Solvent extraction with HP alone was studied earlier (16). It was found that metal extraction can be expressed by

$$Ln^{3+}_{(aq)} + 4HP_{(o)} \overset{K_P}{\rightleftharpoons} LnP_3HP_{(o)} + 3H^{+}_{(aq)}$$

where Ln = Pr, Gd, and Yb, and "aq" and "o" denote the aqueous and organic phases, respectively.

Lanthanide extraction with amine salts was negligible under the experimental conditions of the present study.

The synergistic solvent extraction of Pr, Gd, and Yb with mixtures of HP and several amine salts ($TOAHClO_4$, MDOAHCl, DOAHCl, $DOAHClO_4$) in C_6H_6 was studied using the "slope analysis" method. It is based on an examination of the variation of $D_{P,S}$ (the distribution coefficient due to the synergistic effect) with relevant experimental variables. Log–log plots of $D_{P,S}$ versus one of the variables (pH, [HP], and the concentration of the amine salt [AmHA]) while keeping the other two constant indicates the stoichiometry of the extractable complex. It was found that plots of log $D_{P,S}$ vs pH and log[HP] were linear with slopes close to 4, and plots of log $D_{P,S}$ vs log[AmHA] had slopes close to 1. The experimental data for the metal extraction with mixtures of HP and MDOAHCl are shown in Figs. 1–3.

On the basis of the slope analysis data, metal extraction can be represented by

$$Ln^{3+}_{(aq)} + 4HP_{(o)} + AmHA_{(o)} \overset{K_{P,S}}{\rightleftharpoons} (AmH)[LnP_4]_{(o)} + 4H^{+}_{(aq)} + A^{-}_{(aq)}$$

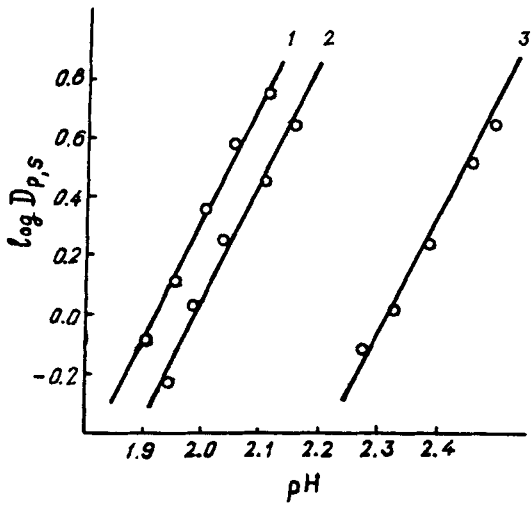

FIG. 1 Log $D_{P,S}$ vs pH for Pr, Gd, and Yb extraction with HP and MDOAHCl at [HP] = 2.5×10^{-2} mol/dm^3 and [MDOAHCl] = 5×10^{-3} mol/dm^3. (1) Yb, (2) Gd, (3) Pr.

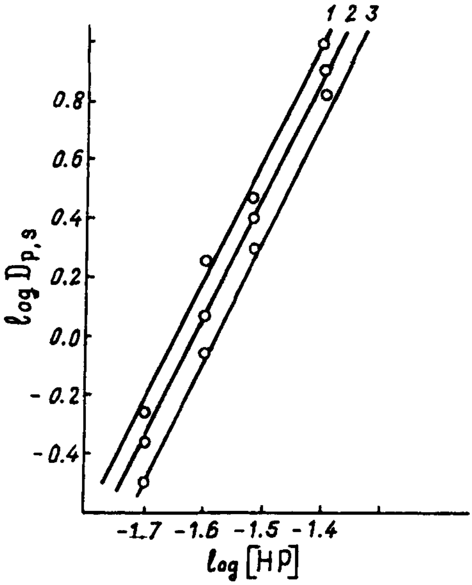

FIG. 2 Log $D_{P,S}$ vs log [HP] for Pr, Gd, and Yb extraction with HP and MDOAHCl at [MDOAHCl] = 5×10^{-3} mol/dm^3. (1) Pr, pH 2.35; (2) Gd, pH 2.00; (3) Yb, pH 1.90.

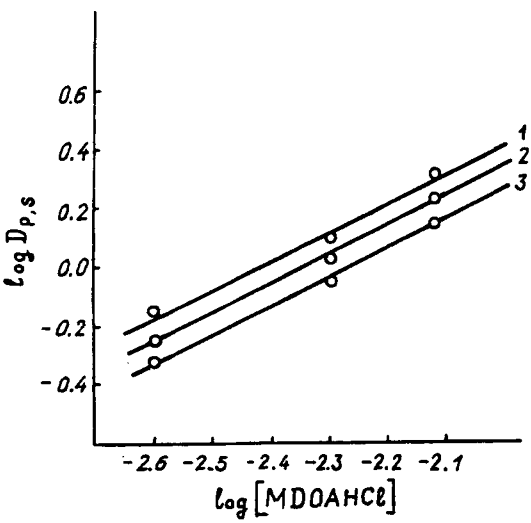

FIG. 3 Log $D_{P,S}$ vs log [MDOAHCl] for Pr, Gd, and Yb extraction with HP and MDOAHCl at [HP] = 2.5×10^{-2} mol/dm^3. (1) Pr, pH 2.35; (2) Gd, pH 2.00; (3) Yb, pH 1.90.

The overall equilibrium constant $K_{P,S}$ can be determined as

$$\log K_{P,S} = \log D_{P,S} - 4\log[HP] - \log[AmHA] - 4\text{ pH} + \log[A^-]$$

The values of the equilibrium constants K_P and $K_{P,S}$ are given in Table 1. The constants K_P and $K_{P,S}$ are concentration constants, i.e., it is assumed that the activity coefficients of the species do not change significantly under the experimental conditions.

Formation of mixed anionic complexes was also found in previous investigations for Pr, Gd, and Yb extraction with HP–TOAHCl, TDDAHCl, $TDDAHClO_4$ (TDDA = tridodecylamine) or methyltricaprylammonium chloride (Aliquat 336, QCl) mixtures (17–20). The values of the equilibrium constant $K_{P,S}$ for these mixtures of extractants are also given in Table 1. The size of the synergistic enhancement can be found by calculation of the synergistic coefficient (S.C.). It was defined by Taube and Siekierski (21) as

$$\text{S.C.} = \log\left(\frac{D_{1,2}}{D_1 + D_2}\right)$$

where D_1, D_2, and $D_{1,2}$ are the distribution coefficients of the lanthanides

TABLE 1
Values of the Equilibrium Constants for Lanthanide Extraction with HP Alone and with Mixtures of HP and Amine Salts

Extractants	Diluents	log K_P; log $K_{P,S}$ Pr	Gd	Yb
HP (16)	CCl_4	−3.60 ± 0.03	−2.56 ± 0.04	−1.76 ± 0.04
	C_6H_6	−4.08 ± 0.05	−3.04 ± 0.04	−2.13 ± 0.04
	$CHCl_3$	−4.63 ± 0.02	−3.79 ± 0.02	−2.61 ± 0.05
HP-TOAHCl (18)	CCl_4	−0.96 ± 0.04	−0.05 ± 0.04	−0.10 ± 0.05
	C_6H_6	−1.54 ± 0.06	−0.40 ± 0.03	−0.25 ± 0.04
	$CHCl_3$	−3.56 ± 0.04	−2.69 ± 0.03	−2.31 ± 0.05
HP-$TOAHClO_4$	C_6H_6	−3.30 ± 0.02	−2.41 ± 0.04	−2.14 ± 0.06
HP-TDDAHCl (19)	C_6H_6	−1.56 ± 0.03	−0.39 ± 0.02	−0.22 ± 0.02
HP-$TDDAHClO_4$ (20)	C_6H_6	−3.35 ± 0.02	−2.48 ± 0.05	−2.23 ± 0.06
HP-MDOAHCl	C_6H_6	−1.57 ± 0.03	−0.15 ± 0.03	−0.04 ± 0.02
HP-DOAHCl	C_6H_6	−1.84 ± 0.03	−0.97 ± 0.04	−0.47 ± 0.04
HP-$DOAHClO_4$	C_6H_6	−3.04 ± 0.03	−2.03 ± 0.03	−1.87 ± 0.03
HP-QCl (17)	CCl_4	0.79 ± 0.01	1.58 ± 0.03	1.67 ± 0.01
	C_6H_6	0.20 ± 0.01	0.81 ± 0.02	0.95 ± 0.01
	$CHCl_3$	−1.86 ± 0.02	−1.08 ± 0.01	−0.90 ± 0.01

between the aqueous and organic phases with the extractants taken separately and with their mixture.

The metal separation can be assessed using separation factors (S.F.). They represent the ratio of the distribution coefficients $D_{P,S}(I)$ and $D_{P,S}(II)$ of the separated metals, i.e.,

$$S.F. = \left(\frac{D_{P,S}(I)}{D_{P,S}(II)}\right)$$

When the two metals form the same type of complexes with a given combination of extractants, the separation factor can be determined as

$$S.F. = \left(\frac{K_{P,S}(I)}{K_{P,S}(II)}\right)$$

For lanthanide extraction with HP alone, the separation factor values can be calculated by the ratio of the respective equilibrium constants $K_P(I)$ and $K_P(II)$.

The values of S.C. and S.F. are given in Table 2. The S.C. values show that the extraction of lanthanides with HP–amine salt mixtures is

TABLE 2

Values of the Synergistic Coefficients (S.C.) and the Separation Factors (S.F.) for Lanthanide Extraction with HP Alone and with Mixtures of HP and Amine Salts

		S.C.			S.F.	
Extractants	Diluents	Pr	Gd	Yb	Gd/Pr	Yb/Gd
HP (16)	CCl_4	—	—	—	11.0	6.3
	C_6H_6	—	—	—	11.0	8.1
	$CHCl_3$	—	—	—	6.9	15.1
HP-TOAHCl (18)	CCl_4	5.34	4.20	3.56	8.1	1.4
	C_6H_6	4.24	4.34	3.57	13.8	1.4
	$CHCl_3$	2.76	2.81	2.00	7.4	2.4
HP-TOAHClO$_4$	C_6H_6	2.48	2.35	1.68	7.8	1.9
HP-TDDAHCl (19)	C_6H_6	4.22	4.35	3.60	14.8	1.5
HP-TDDAHClO$_4$ (20)	C_6H_6	2.43	2.26	1.59	7.4	1.8
HP-MDOAHCl	C_6H_6	4.21	4.61	3.87	26.3	1.5
HP-DOAHCl	C_6H_6	3.94	3.77	3.55	7.4	3.1
HP-DOAHClO$_4$	C_6H_6	2.74	2.71	1.95	10.2	1.4
HP-QCl (17)	CCl_4	6.08	5.84	5.11	6.2	1.2
	C_6H_6	5.98	5.56	4.78	4.1	1.4
	$CHCl_3$	4.46	4.41	3.41	6.0	1.5

connected with a rather large enhancement. The largest S.C.s were established for HP–QCl mixtures in CCl_4. The S.C. values decrease with a change of the diluent and the anion of the amine salt in the sequence $CCl_4 > C_6H_6 > CHCl_3$ and $Cl^- > ClO_4^-$, respectively. The data in Table 2 show that, as a whole, the chelating extractant alone give better possibilities for lanthanide separation than mixtures of HP and amine salts, especially for the Gd/Yb pair. Although the synergistic mixtures usually do not give better separation than the chelating extractant, there are some mixtures of extractants, e.g., HP–TOAHCl, HP–TDDAHCl, and HP–DOAHCl in C_6H_6, which combine rather large synergistic coefficients with rather large separation factors for the Pr/Gd pair. The best separation of the Pr/Gd pair is reached when the HP–MDOAHCl mixture in C_6H_6 is used. Therefore, on the basis of the experimental data, it is concluded that separation of the lighter lanthanides can be improved by using a mixture of HP and MDOAHCl, but that a better separation of the heavier lanthanides can be reached using HP alone.

CONCLUSIONS

Pr, Gd, and Yb are synergistically extracted with HP–amine salt mixtures as $(AmH)[LnP_4]$ species. The anion of the salt exerts a considerable influence on lanthanide extraction. The largest synergistic coefficients are found for the HP–QCl combination. The other amine salts cause lower synergistic enhancement. The synergistic mixtures give a worse separation of lanthanides than the chelating extractant. However, some mixtures involve a combination of high S.C. and a rather high S.F. for the Pr/Gd pair.

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Received by editor August 5, 1996
Revision received February 1997