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SOLVENT EXTRACTION OF LANTHANIDES WITH 1-PHENYL-3-METHYL-4-BENZOYL-5-PYRAZOLONE

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ABSTRACT

The solvent extraction behavior of 13 lanthanides has been investigated using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HP) as an extractant in aqueous-benzene medium. The composition of the extracted species has been determined as $LnP_3 \cdot HP$. The values of the equilibrium constant as well as the separation factors between the adjacent elements have been evaluated.

Key Words: Liquid–liquid extraction; 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone; Lanthanides separation factors

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INTRODUCTION

The class of chelating extractants which have received the most attention in recent years have the basic structure of 4-acylpyrazolones.[1–3] Because of their increased acidity (relative to β-diketones) and various synthetic modifications, which can be made to the basic structure, these extractants present some possibilities for improved separation procedures for the f-elements.[4] This is of great interest for the treatment and recycling of industrial wastes and particularly nuclear ones. Among the most difficult of separations of metal ions are the intra- and inter-group separation of lanthanides and trivalent actinides. 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HP) has been extensively studied alone[5] or in combination with other reagents in the extraction of f-elements,[6–11] divalent transition metals,[12–14] and alkali or alkaline earth metals.[15]

Most of the previous investigations deal with the extraction of some rare earth ions but there is no systematic study on the extraction behavior of the entire rare earth series using HP in aqueous-benzene medium. So, the present work was undertaken in order to study the extraction of the lanthanide metals (with the exception of Ce because its unstable trivalent state and the radioactive Pm) from the above extraction system and to determine the possibilities for the separation of the lanthanides.

EXPERIMENTAL

The commercial compound HP with purity $>99\%$ (Fluka) was used as received and the diluent was benzene (Merck, p.a.).

The 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.

The experiments were carried out using 10 mL volumes of aqueous and organic phases. The samples were shaken mechanically for 60 min at room temperature which was sufficient to attain equilibrium. After the separation of the phases, the metal concentration in the aqueous phase was determined photometrically using Arsenazo III.[16] The acidity of the aqueous phase was measured using a pH-meter with an accuracy of 0.01 pH unit. The ionic strength was maintained at $0.1\,M$ with (Na,H)Cl. The initial concentration of the metals was $2.5 \times 10^{-4}\ \mathrm{mol/dm^3}$.

RESULTS AND DISCUSSION

A traditional and effective means of obtaining both stoichiometric and equilibrium constant information about extraction processes, called “slope analysis," is based on an examination of the variation of D, the distribution ratio, as a function of the relevant experimental variables. A log–log plot of the extraction data in the form of D vs. pH and [HP] 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 hydrolysis in the aqueous phase as well as 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 13 rare-earth metals with HP are shown in Figs. 1 and 2. The plots of $\log D_p$ vs. pH are linear with slopes close to three and the plots of $\log D_p$ vs. $\log\,[\mathrm{HP}]$ show slopes close to four.

On the basis of slope analysis data, the solvent extraction of the lanthanides can be described by the equation:

$$\mathrm{Ln}^{3+}_{(aq)} + 4\mathrm{HP}_{(o)} \overset{K_p}{\Leftrightarrow} \mathrm{LnP_3{\cdot}HP}_{(o)} + 3\mathrm{H}^{3+}_{(aq)} \tag{1}$$

where Ln denotes lanthanides and "aq" and "o" the aqueous and organic phase, respectively.

The overall equilibrium constant K_p can be determined as

$$\log K_p = \log D_p - 3\,\mathrm{pH} - 4\log\,[\mathrm{HP}] \tag{2}$$

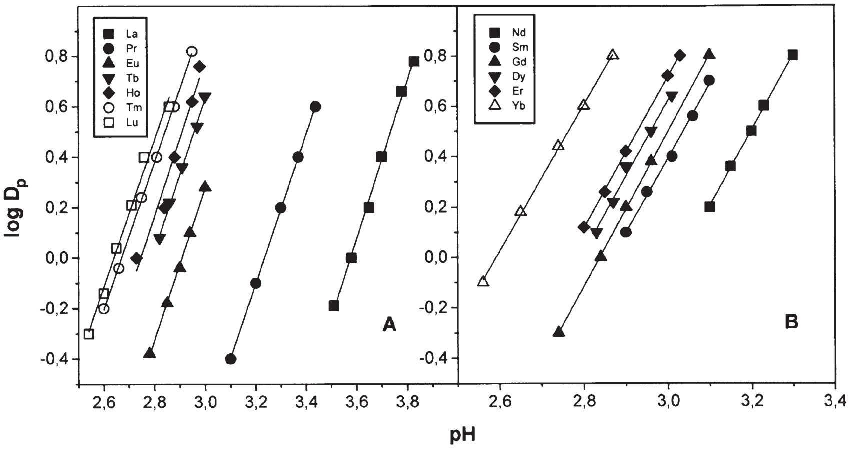

Figure 1. Log D_p vs. pH for the extraction of lanthanide elements having (A) odd atomic number and (B) even atomic number with HP in benzene at $[\mathrm{HP}] = 4 \times 10^{-2}\ \mathrm{mol/dm^3}$.

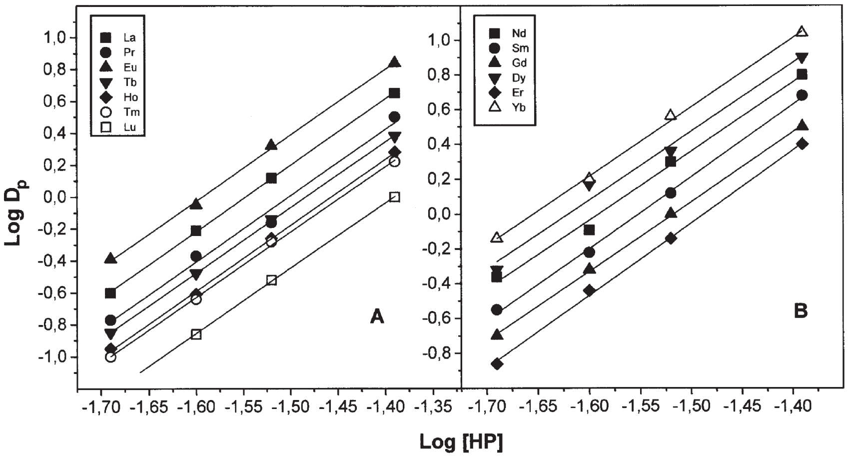

Figure 2. Log D_p vs. log [HP] for the extraction of lanthanide elements having: (A) odd atomic number, La (pH = 3.80), Pr (pH = 3.40), Eu (pH = 3.20), Tb (pH = 2.90), Ho (pH = 2.85), Tm (pH = 2.75), Lu (pH = 2.65); (B) even atomic number, Nd (pH = 3.30), Sm (pH = 3.10), Gd (pH = 3.00), Dy (pH = 3.10), Er (pH = 2.90), Yb (pH = 2.95).

The values of log K_p are given in Table 1. It is seen that they increase with an increase in the atomic number of the lanthanides as expected from their decreasing atomic radii.

The formation of self-adducts $LnP_3{\cdot}HP$ when pyrazolone is used as extractant was found in some other studies[17–20] but in Refs. [4,5,21] extraction of LnP_3 chelate complex was reported. This discrepancy is probably due to the fact that the dependency of log D_p vs. log [HP] has not been investigated by some authors.[22]

The structure of the self-adducts could be compared with those of the mixed synergistic complexes. As far as 40 years ago Irving and Edgington[23] noticed that the chelating extractant neutralizes the charge of the metal ion and the second extractant (synergist) coordinates to the metal displacing residual water molecules and rendering the synergistic complex less hydrophilic. It can be expected that the self-adduct $LnP_3{\cdot}HP$ are more hydrophobic than the metal chelate LnP_3 as the three pyrazolone anions neutralize the charge of the lanthanide cation and the fourth neutral molecule HP probably displaces the water molecules from the inner coordination sphere. So, the self-adducts formation can produce an increase in the synergistic mixtures of extractants. Such an effect can be named as self-synergism.

Table 1. Values of the Equilibrium Constants K_p and SF for the Lanthanide Extraction with HP in C_6H_6

Metal	Log K_p	SF
La	− 5.26	
Pr	− 4.08[8]	15.12
Nd	− 3.50	3.80
Sm	− 3.12	2.39
Eu	− 2.99	1.35
Gd	− 3.04[8]	0.89
Tb	− 2.80	1.73
Dy	− 2.76	1.10
Ho	− 2.69	1.17
Er	− 2.64	1.12
Tm	− 2.42	1.65
Yb	− 2.13[8]	1.95
Lu	− 2.19	0.87

Error limits in the range ± 0.08.

The separation of the lanthanide metals using HP can be assessed by the separation factors (SF). They represent the ratio of the distribution coefficients of two adjacent lanthanides viz. $D_p(z+1)$ and $D_p(z)$. When the two metals form the same type of complexes, the SF can be determined as

$$\mathrm{SF} = K_p(z+1)/K_p(z) \tag{3}$$

The values of the SF of the studied metals are given in Table 1.

The separation factor between La and Lu is approximately 1.2×10^3, which is similar to those found for the extraction of the lanthanides with HP ($\sim 10^3$) in aqueous-chloroform medium.[5] It is relevant at this stage to point out that the type of usable diluents (polar-$CHCl_3$, or nonpolar-C_6H_6) does not have too much importance on the separation efficiency between the metals. The values for the SF for the Eu–La (186.1) and Lu–Eu (6.3) pairs remains almost the same as those obtained for HP in xylene[20] as well as for 4-Acylpyrazolone derivatives in chloroform.[4]

It should also be noted that a loss of separation selectivity is observed across the 4f series. The selectivity for light/heavy intra-group separations may be derived from the tendency of the pyrazolones to form more easily self-adducts with the light members. Presumably, the light/heavy fractionation results from steric restriction caused by the shrinking radii of the heavier members. The cation radii decrease by roughly 20% across the series. The effects of lanthanide and actinide separation have been discussed thoroughly in the Nash review.[7]

CONCLUSION

The solvent extraction of thirteen lanthanide metals with HP in C_6H_6 has been studied. The experimental data showed that self-adducts $LnP_3{\cdot}HP$ are formed. The structure of these complexes can be compared with those of the synergistic complexes as the fourth ligand (HP) coordinated to the metal can play the role of the second extractant in the synergistic extraction system and replace residual water molecule from the inner coordination sphere of the chelate LnP_3.

The SF between the adjacent metals are not high. Still, their values are much larger for the light lanthanides.

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