Studies on the solvent extraction of trivalent lanthanides with hexafluoroacetylacetone (HFAA) and tri-*n*-octylphosphineoxide (TOPO)

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Abstract. Trivalent lanthanides can be synergistically extracted from aqueous solution as mixed ligand complexes with HFAA and TOPO with the general formula, $Ln(HFAA)_3 \cdot 2TOPO$. The optimum conditions for extraction like equilibration time, pH, effect of solvent, metal ion concentration, and reagent concentration were established. The solvent extraction by mixed ligand system can be used for the preparation of volatile gas chromatographable lanthanide complexes.

Keywords. Synergic extraction; mixed ligand complexes; trivalent lanthanides.

1. Introduction

Solvent extraction enables quantitative separation of metal chelates into organic phase [1,2]. Hexafluoroacetylacetone, $CF_3 - C(=O)-CH_2-C(=O)-CF_3$, (HFAA), forms hydrated chelates with rare earths, which are poorly extractable [3]. Neutral donors like TOPO, TBP, DBSO etc. are known to act as synergistic agents and enhance percentage extraction of metal chelates [4]. To develop a best solvent extraction system for the preparation of gas chromatographable volatile complexes of lanthanides using HFAA and TOPO, the authors made systematic and detailed studies and these results are presented in this paper. The optimum conditions were established for achieving effective separation of complex group of rare earth elements considering entire rare earths into two groups. The first group consists of lighter elements (La, Ce, Pr, Nd, Sm and Eu) while the second group consists of the remaining rare earths (Gd, Tm, Dy, Ho, Er and Lu).

2. Experimental

2.1 *Reagents*

The lanthanide oxides (M/s Indian Rare Earths Ltd, 99·9% purity) were dissolved in 0·01 M hydrochloric acid and standardised by titrating with EDTA using xylenol orange as an indicator [5].

 0·1 M solution of hexafluoroacetylacetone (M/s Fluka, Switzerland) and tri-*n*-octylphosphine oxide (M/s E-Merck) were prepared using cyclohexane as a diluent.

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2.2   *Solvent extraction procedure*

5 ml of the 0·01 M lanthanide ion solution was placed in a separating funnel and the acidity was adjusted to 0·01 M HCl and the total volume made up to 10 ml. 10 ml portions of cyclohexane with 0·1 M HFAA and 0·1 M TOPO were added to the separating funnel, stoppered and shaken for 15 min. The phase separation was achieved by centrifugation and percent extraction was determined by titration of aqueous phase with EDTA using xylenol orange as an indicator.

3.   Results and discussion

Detailed experimental studies of solvent extractions were carried out on typical lanthanides, neodymium (representative of lighter lanthanides) and dysprosium (representative of heavier lanthanides) for establishing optimum conditions for extraction.

3.1   *Effect of equilibration time and acidity/pH*

A 10-minute equilibration time was found to be enough quantitatively to extract all the lanthanides. Quantitative extraction can be achieved from 0·001–0·04 M hydrochloric acid or nitric acid for all lanthanides with fixed concentration of HFAA and TOPO whereas with sulphuric acid and perchloric acid, the extraction was not quantitative and non-reproducible results were observed, particularly in high acid medium. Studies on the dependence of percentage extraction on *pH* indicated that quantitative extraction of lanthanide ions could be achieved from *pH* 2 to 7.

3.2   *Effect of solvent*

Of the organic solvents such as cyclohexane, hexane, benzene, carbon tetrachloride, chloroform and methylisobutylketone, tested cyclohexane was found to be the best solvent for the quantitative extraction of lanthanides. The distribution coefficients of lanthanide complexes of HFAA-TOPO system at *pH* 2·0 into different non-polar solvents were found to be in the same order of the solubilities of these solvents in water (table 1). With more polar solvents like hexone or chloroform, low percentage

Table 1.   Correlation of metal distribution coefficient with water solubility of diluent
Aqueous phase: 5·0 ml of 0·01 M Ln(III) solution; acidity 0·01 M hydrochloric acid. Total volume made up to 10·0 ml
Organic phase: 10·0 ml of cyclohexane with 0·1 M HFAA and 0·1 M TOPO

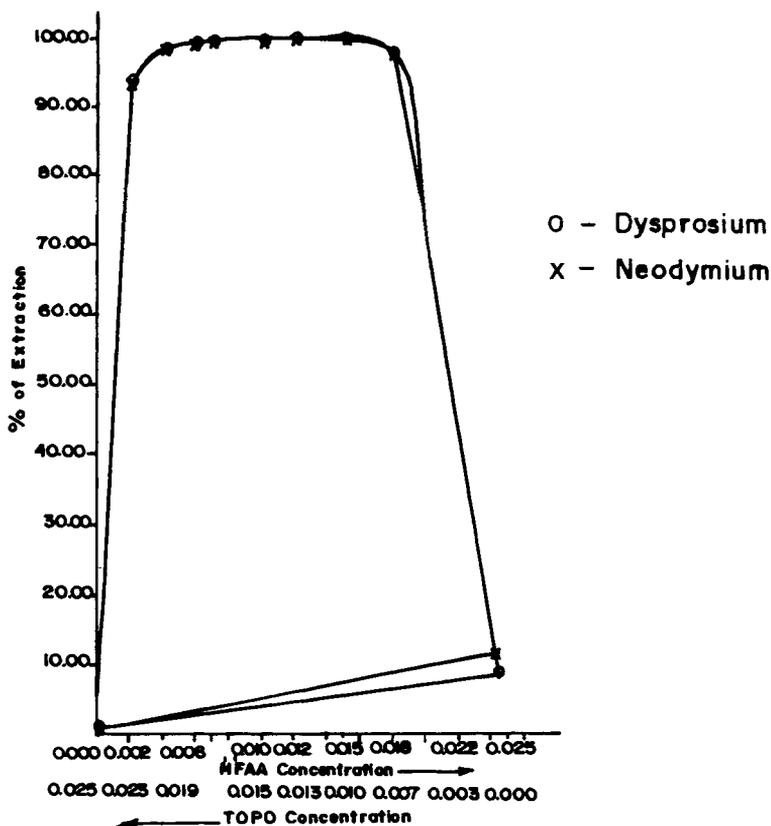|	Distribution coefficient of Ln–HFAA–TOPO system		Water solubility of pure diluent (g/l)
Diluent	Nd	Dy	
Cyclohexane	$1·0 \times 10^3$	$0·97 \times 10^3$	0·04
Hexane	$0·90 \times 10^3$	$0·92 \times 10^3$	0·07
Carbontetrachloride	$8·85 \times 10^2$	$8·76 \times 10^2$	0·12
Benzene	$6·51 \times 10^2$	$6·48 \times 10^2$	0·54
Chloroform	$5·5 \times 10^2$	$5·45 \times 10^2$	1·30
Hexone	$5·0 \times 10^2$	$5·0 \times 10^2$	16·0

Figure 1. Synergistic effect on the extraction of lanthanides due to HFAA/TOPO mixtures. O Dysprosium; X Neodymium.

extraction of lanthanide-HFAA-TOPO system was observed which may be due to the greater dipole-dipole interaction between polar solvents and HFAA-TOPO reagent system than with non-polar solvents like cyclohexane.

3.3 *Effect of reagent concentration*

Extraction studies were performed using varying concentrations of HFAA and TOPO in cyclohexane from 0·01 M hydrochloric acid containing lanthanide ion solutions. Very high synergic effect in the extraction was observed (figure 1) which was evident from the large increase in percentage extraction of the mixed ligand complexes HFAA and TOPO system when compared to the individual ligands.

3.4 *Nature of extraction species*

To obtain information on the possible species being extracted into the cyclohexane phase, the three variables in the system [H^+], HFAA and TOPO were examined, keeping two constant at a time. As expected from trivalent metal-HFAA system, it was found that on keeping H^+ and TOPO concentration constant, while varying the HFAA concentration, a log/log plot of partition coefficients of lanthanide ions against HFAA concentration gave a straight line of slope 3. A similar log/log plot varying only

H^+ concentration gave a line of slope 3. On keeping both H^+ and HFAA concentration constant, variation of TOPO concentration gave a line of slope 2.

Based on the above data, the formation of the mixed-ligand complex can be represented by the following reaction

$$[Ln^{3+}] + 3[HHFAA] + 2[TOPO] \rightarrow [Ln(HFAA)_3 \cdot 2TOPO] + [H^+].$$
(1)
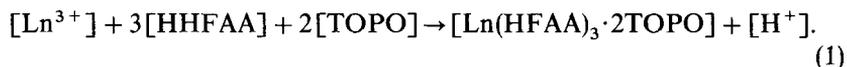
When the initial concentration of the HFAA was kept in-constant excess, and the concentration of H^+ was maintained at a low level (0·01 M), the equilibrium was shifted to the right and the amount of TOPO becomes the limiting quantity in the extraction. Maximum percent extraction will therefore occur when the stoichiometric amount of TOPO at 2 was added.

3.5 *Effect of ionic size on the extraction of trivalent lanthanide ions*

To understand the influence of ionic size of the metal ion on its extraction with HFAA-TOPO system the percentage extraction of all the trivalent lanthanide ions along with scandium and yttrium ions with fixed limited concentrations of HFAA (3 times) and TOPO (2 times) was studied (table 2 and figure 2). From these data the following observations can be made.

● Extraction of the rare earths reaches a maximum at Eu or Sm, which lie near the middle of the lanthanide series
● the extraction of scandium is higher than that of all the rare earth ions, although it exceeds that of Eu and Sm by only a small amount
● the extraction of yttrium is similar to that of erbium and thulium in all cases.

The above features can be explained in terms of the known chemistry of the trivalent rare earth metal ions. The complexes formed by all the rare earth metals tend to be largely ionic in nature. Owing to the poor mutual shielding of the 4f electrons, each

Table 2. Extraction of rare earth ions as HFAA-TOPO mixed ligand complexes

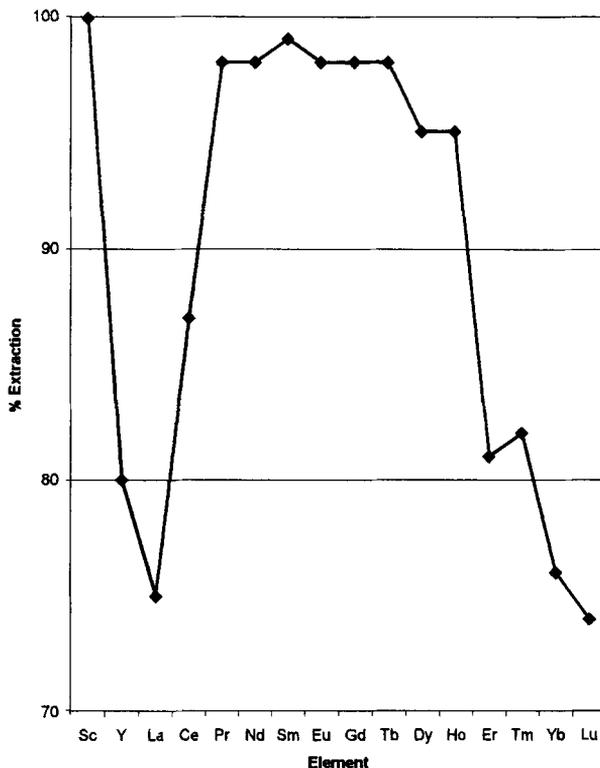| Element	Ionic radius (Å)	%Extraction
Sc	0·68	99·9
Y	0·88	80·0
La	1·061	75·0
Ce	1·034	87·0
Pr	1·013	98·0
Nd	0·998	98·0
Sm	0·964	99·0
Eu	0·950	98·0
Gd	0·938	98·0
Tb	0·923	98·0
Dy	0·908	95·0
Ho	0·894	95·0
Er	0·881	81·0
Tm	0·869	82·0
Yb	0·858	76·0
Lu	0·848	74·0

Figure 2. Extraction of rare earths as HFAA-TOPO mixed ligand complexes.

successive electron experiences a gradual increase in effective nuclear charge, with the result that 4f shell (and hence the ionic radius) decreases markedly in size through the series from lanthanum (0, 106 nm) to lutecium (0, 085 nm). Since the electrostatic interaction between the cation and the ligand should be proportional to the reciprocal of the cationic radius, the stabilities of ionic complexes would be expected to increase through the series from trivalent lanthanum to lutecium which may result in increase in percentage extraction with decreasing ionic radius. Such an increase is often observed only for the lighter lanthanides. Once the cationic radius diminishes to a limiting size to that of Eu or Sm the steric factors become significant such that any decrease in the radius cannot accommodate the three HFAA molecules and two TOPO molecules. Thus, the heavier of lanthanides do become too small in their ionic radius to accommodate all the HFAA and TOPO ligands with a consequent reduction in the stability of the complexes which may be due to decrease in the coordination number of lanthanide ion or increase in significance of steric factors, or both [6]. It can be seen that maximum extraction is achieved for dysprosium, europium, gadolinium and neodymium with fixed limited concentration of HFAA (3 times) and TOPO (2 times) when compared to other lanthanides.

4. Conclusions

It was observed that by solvent extraction, mixed ligand complexes of lanthanides, $Ln(HFAA)_3 2$. TOPO can be efficiently separated from interfering with major matrix

elements and the pure solid volatile mixed complexes can be rapidly prepared by evaporating the extractant and recrystallisation. Further, the extact of the mixed ligand complex of lanthanides can be directly fed into gas chromatograph for the separation of individual lanthanides and their estimation.

Acknowledgements

References

1. Lin Y, Brauer R D, Laintz K E and Wai C M 1993 *Anal. Chem.* **65** 2549
2. Lin Y and Wai C M 1994 *Anal. Chem.* **66** 1971
3. Butts W C and Banks C V 1970 *Anal. Chem.* **42** 133
4. Burgett C A and Fritz J S 1972 *Anal. Chem.* **44** 1738
5. Kinnenen J and Wennerstand B 1957 *Chemist-Analyst* **46** 92
6. Moeller T 1973 In *Comprehensive inorganic chemistry* (eds) J C Bailaae, H J Emeleus, R Nyholm and A F Trotman (Oxford: Pergamon) p. 28