RADIOCHEMICAL STUDY OF THE SEPARATION OF CERIUM(III)
FROM LANTHANUM BY SOLVENT EXTRACTION USING N-BENZOYL-
N-PHENYLHYDROXYLAMINE

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The extraction of cerium(III) and lanthanum(III) by N-benzoyl-N-phenylhydroxyl-
amine (N-BPHA) in chloroform has been studied in order to determine the com-
position and extraction constants of the extracted chelates. From the results obtained,
the best conditions for the separation of cerium from lanthanum (separation factor
about 200) have been predicted and experimentally verified.

Introduction

Various methods (precipitation, ion exchange and solvent extraction have been
described for the separation of Ce from La. The separation factors were usually
small (from 1 to 10), and for this reason the effective separation of the metals
was impossible in a few separation steps. In the present paper the extraction of
Ce(III) and La(III) by N-BPHA solution in chloroform has been investigated
in order to determine the extraction constants and to find the best conditions
for their separation. Recently, a paper dealing with the extraction separation of
La from Ce(IV) using N-BPHA was published by Murugaiyan and Das, but somewhat different conditions were used.

Theoretical

The extraction of lanthanides with N-BPHA is generally described by the
following reaction:

\[ M^{3+} + (3 + x)(HA)_{org} = (MA_3(HA)_x)_{org} + 3H^+ \]  

(1)

where HA is an undissociated and A\(^-\) a dissociated molecule of N-BPHA. The
equilibrium constant of this reaction (the extraction constant) \( K \) is:

\[ K = \frac{[MA_3(HA)_x]_{org} [H^+]^3}{[M^{3+}] [HA]^{3+x}_{org}} = q_0 \frac{[H^+]^3}{[HA]^{3+x}_{org}} \]  

(2)
where \( q_0 \) is the equilibrium ratio of the investigated lanthanide and \([HA]\)\(_{\text{org}}\) is the equilibrium concentration of N-BPHA in the organic phase. Because of the formation of hydroxo complexes in the aqueous phase, the experimentally determined distribution factor \( q \) is expressed by:

\[
q = \frac{[MA_3(HA)]_{\text{org}}}{[M^{3+}] + [M(OH)^{2+}] + [M(OH)]_{\text{org}} + \ldots} = \\
= \frac{\text{K}[HA]_{\text{org}}^{3+x}}{[H^+]^3 (1 + *K_1[H^+]^{-1} + *K_1 *K_2[H^+]^{-2} + \ldots)} = \\
= \frac{\text{K}[HA]_{\text{org}}^{3+x}}{[H^+]^3 (1 + \sum_{n=1}^{\infty} \prod_{n=1}^{\infty} *K_n)}
\]

(3)

where \(*K_n = \frac{[M(OH)]_{n-1}^{3-n} [H^+]^{n}}{[M(OH)]_{n-1}^{3-n} \text{[M(OH)]}}\) are the \( n \)-th acid dissociation constants for the hydrolysis of a lanthanide ion.

From Eq. (3) the extraction constant \( K \) can be calculated by determining \( q \) at different \( pH \) values and different equilibrium concentrations of the reagent in the organic phase.

The separation factor, \( \alpha \), is related to the individual distribution factors as follows:

\[
\alpha = \frac{q_{(1)}}{q_{(2)}} = \frac{K_{(1)}}{K_{(2)}} [HA]_{\text{org}}^{x_{(1)}-x_{(2)}} \left( 1 + \sum_{n=1}^{\infty} \prod_{n=1}^{\infty} *K_{n(2)} \right) \\
(1 + \sum_{n=1}^{\infty} \prod_{n=1}^{\infty} *K_{n(1)})
\]

(4)

where \( q_{(1)}, q_{(2)} \) are the distribution factors of the metals \( M_{(1)} \) and \( M_{(2)} \), respectively. From Eq. (4) it is evident that the separation of two elements can be achieved by the change of the concentration of the reagent \([HA]\)\(_{\text{org}}\) when \( x_{(1)} \neq x_{(2)} \), even in the case when the extraction constants are identical. For example, for the extraction of more than 95\% of metal \( M_{(1)} \) and less than 0.1\% of metal \( M_{(2)} \) present originally at the same concentrations, the following equations are valid (for \( x_{(1)} < x_{(2)} \), \( K_{(1)} \sim K_{(2)} \) and \( V_{\text{org}} = V_{\text{aq}} \)):

\[
\left( \frac{q_{(1)}}{q_{(1)} + 1} \right)^x \geq 0.95
\]

(5)