THERMODYNAMICS OF THE EXTRACTION OF EUROPIUM(III) RADIOTRACER BY BENZYL-PHOSPHONIC ACID MONOESTER

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The extraction of Eu$^{3+}$ from perchloric acid by ethyl hydrogen benzyl phosphonate (HEBP) dissolved in a series of organic diluents, has been studied at different temperatures. From the variation of the distribution ratio with temperature, the thermodynamic functions $\Delta H$, $\Delta S$ and $\Delta G$ have been determined. The meaning of the experimentally obtained thermodynamic quantities is discussed.

Introduction

Phosphonic acid monoesters of the type (R'O) (R)PO(OH), where R, R' may be alkyl or aryl groups were studied as possible extractants for transition elements.\textsuperscript{1-3} Such compounds may coordinate as polydentate ligands.

This paper deals with the extraction of Eu$^{3+}$ by ethyl hydrogen benzyl phosphonate (C$_2$H$_5$O) (C$_6$H$_5$CH$_2$) PO (OH) dissolved in organic solvents of different dielectric constants from aqueous perchlorate solution at constant ionic strength $M = 1$ (Na$^+$, HCIO$_4$) and pH 2.5 at different temperatures. The extraction stoichiometries are suggested and the thermodynamic parameters are evaluated.

Experimental

Chemicals and radiotracer

Unless otherwise stated, the chemicals used were of AR purity grade. The extractant, ethyl hydrogen benzyl phosphonate, was synthesized and purified as described in a previous work.\textsuperscript{4} The organic solvents: benzene, nitrobenzene, n-hexane, carbon tetrachloride and chloroform were products of B.D.H. and used without further purification.
The radiocative tracer Eu (152 + 154) was prepared locally by thermal neutrons irradiation of its spectroscopically pure oxide in the ET-RR-1 reactor of the Egyptian Atomic Energy Authority. The oxide was dissolved in HCl and the chloride was transformed into perchlorate by successive evaporation and dissolution in dilute HClO₄ to give a 10⁻⁶M solution. The ionic strength was adjusted to $M=1$ and pH at 2.5 by NaClO₄ and HClO₄.

Procedure

In all cases, the organic phase was pre-equilibrated with aqueous medium having an ionic strength of 1.0 (H⁺, NaClO₄) and adjusted to the required pH using HClO₄. Partition investigations were carried out by shaking equal volumes of the organic and the aqueous phases at the required temperature ($t\pm0.1$ °C) for one hour, time enough for equilibrium, after which the phases were separated by centrifugation and the pH of the aqueous solution was measured with a pH-meter of type Unicam 900 MK2 expandable scale, connected to 2 combined glass electrodes. The europium concentrations in both phases were determined radiochemically by measuring the Eu(152 + 154) activity using Na(Tl) scintillation counter (ECKO). The distribution ratio (D) of the metal was thus given by the ratio of the activity in the organic phase to the activity in the aqueous phase.

Results and discussion

A typical set of extraction data is represented graphically in Fig. 1, which shows the effect of varying the pH of the aqueous phase on the distribution ratio, $D$, of Eu₃⁺ at constant ionic strength $\mu=1.0(\text{HClO}_4-\text{NaClO}_4)$ and at 25 ± 0.1 °C. The concentration of HEBP was $1\cdot10^{-2}$M in n-hexane. The data were fitted by a computer program, applying the least squares method. A linear relation is observed with a slope of 3, which is the charge carried by the extracted ion.

The effect of varying the concentration of HEBP in the five organic solvents on the extraction of Eu₃⁺ from the same aqueous phase of ionic strength $\mu=1.0$ (Na⁺, HClO₄) at pH 2.5 and 25 ± 0.1 °C was carried out. The results are represented in Fig. 2, where straight lines with positive slopes of 3 can be observed.

Based on these results, the following equation describes the extraction of Eu₃⁺ in the different solvents investigated under the conditions of the experiment:

$$\text{Eu}^{3+} + 3(\text{HEBP})_2 \rightleftharpoons \frac{K}{\text{Eu(EBP)}_3(\text{HEBP})_3 + 3H^+}$$