REGULARITIES OF EXTRACTION OF URANYL THENOYLTRIFLUOROACETONATE INTO A NUMBER OF SOLVENTS

K. AKIBA, N. SUZUKI,* H. ASANO, T. KANNO

Research Institute of Mineral Dressing and Metallurgy,
Tohoku University, Sendai (Japan)

(Received August 28, 1970)

The extraction equilibria were investigated of the thenoyltrifluoroacetone (TTA) chelate of uranyl ion between aqueous perchlorate medium and thirteen organic solvents. The extracted species was shown to be UO$_2$A$_2$. The solubility parameter of the chelate was estimated from the partition data and it was confirmed that the relationship $\lg P_M = n \lg P_{HA} + \text{const.}$ holds for the present system. When the extraction constant ($K_{ex}$) is considered in relation to the distribution coefficients, the $K_{ex}$ values are expected to be constant under certain conditions for all of the solvents; the $\lg K_{ex}$ values were found to be constant ($\lg K_{ex} = -2.85 \pm 0.17$).

Introduction

Together with advances in the chemistry of uranium complexes, much progress has been made in solvent extraction. Extraction methods are widely applicable to the separation of a variety of materials; however, few systematic studies have been undertaken to explain the roles of the solvents in the extraction processes. Elucidation of solvent effects will lead to information which is important not only as regards an effective separation but also with regard to research work in the field of solution chemistry. In previous papers, regularities in distribution were explained with the aid of the solubility parameter concept in typical chelate extraction systems.$^{1,2}$ Further, the effect of solvents on the adduct formation between a chelate and neutral ligand was clarified by considering the activity coefficients of species in various organic solutions.$^2$

The present study was undertaken to clarify the effects of the solvents on the extraction of the thenoyltrifluoroacetone (TTA) chelate of uranyl ion. The extraction mechanism was investigated and the distribution coefficients of the chelate were obtained in several 'inert' solvents. The extraction regularities were considered in connection with the equilibrium constants in the extraction processes.

* Present address: Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan.
Experimental

Tracer

$^{237}\text{U}$ was prepared by ($\gamma$, n) reaction on $^{238}\text{U}$. A mixture of triuranium octoxide (0.1 g) and graphite (0.5 g) enclosed in a quartz ampoule was irradiated for several hours with a 40~60 MeV bremsstrahlung from a linear electron accelerator in the Laboratory of Nuclear Science, Tohoku University. After the irradiated sample had been dissolved in hot 6M nitric acid, the graphite carrying fission products was removed by filtration; the filtrate was shaken with 50% (v/v) tributyl phosphate in toluene, and the organic layer was washed with 2M HNO$_3$. The uranyl species was transferred into an aqueous phase by shaking with water after the TBP solution had been diluted 10-fold by volume with benzene. The specific activity of the uranium isotope was sufficiently high for this investigation.

Materials

TTA was purified by sublimation under reduced pressure and dried over phosphorus pentoxide. All solvents used were of the highest purity commercially available, and were further purified by the usual means.

Method

A perchloric acid solution containing $^{237}\text{U}$ ($T = 6.75$ d), with pH in the range 1 to 4, was shaken for 20 hrs with an equal volume of TTA solution. The ionic strength was maintained at 0.10 with sodium perchlorate. The two phases were separated by centrifuging, and the $\gamma$-activity of each phase was measured with a well-type NaI(Tl) scintillation counter. The pH of the aqueous residue was measured. All experiments were carried out in a room thermostatted at 25 ± 1 °C.

Results and discussion

Extraction equilibria

Extraction equilibria can be formally written in the following steps. The distribution of TTA(HA) is defined by:

$$\text{HA}_{\text{aq}} \rightleftharpoons \text{HA}_{\text{org}}; \quad P_{\text{HA}}$$ (1)

where the subscripts org and aq stand for the species in the organic and aqueous phases, respectively. The symbols on the right represent the equilibrium constants of each step. The acid dissociation of HA is:

$$\text{HA}_{\text{aq}} \rightarrow \text{H}^+ + \text{A}^-; \quad K_a$$ (2)

The formation of the chelates of the uranyl ion is expressed by:

$$\text{UO}_2^{2+} + n \text{A}^- \rightleftharpoons \text{UO}_2\text{A}_{n,\text{aq}}^{(2-n)+}; \quad \beta_n$$ (3)

J. Radioanal. Chem. 7, 1971