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TECHNICAL NOTE

Extraction of Uranium from "Abu-Tartur" Phosphate Aqueous Leachate Solution

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ABSTRACT

Uranium was effectively extracted from a synthetic aqueous monocalcium phosphate/phosphoric acid mixture (MCP/H_3PO_4) by tri-*n*-octylamine dissolved in different solvents and the presence of low concentrations of some counteranions (oxalate, citrate, chloroacetate) in the aqueous phase. The extraction efficiency was markedly enhanced by the salting out action of the concentration of calcium ions in the MCP/H_3PO_4 solution.

Key Words. Uranyl ion; Phosphate ore; Solvent extraction; Anionic carboxylate complexes

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INTRODUCTION

In the future, phosphate rock may be an important source of uranium because of the limited availability of high grade ores and because uranium removal may become compulsory to avoid its dissemination to the environment during the application of phosphate-based fertilizers. The particular process for recovery of uranium from its ores depends on the nature of the ore. "Abu-Tartur" phosphate deposits are in the form of carbonate fluoroapitite, $Ca_5(PO_4)_3F_n(CO_3)_{1-n}$, with a uranium content of 40–50 ppm (1). All the processes include a leaching step that solubilizes the metal. Solvent extraction is used most frequently for the recovery of uranium from the leach liquor (2–4). The nature of the extractant depends on the type of the lixiviant used to leach the ore. Presently most uranium ores are leached by sulfuric acid in the presence of an oxidizing agent. The preferred extractants are long-chain amines or a mixture of di-(2-ethylhexyl) phosphoric acid (HDEHP) and tributyl phosphate (TBP) or trioctyl phosphine oxide (TOPO) (5–12).

In this work U(VI) ions are selectively extracted from the MCP/H_3PO_4 mixture as anionic complexes of oxalate, citrate, or trichloroacetate by tri-*n*-octylamine in different solvents. The equilibrium time, counteranion concentration, extractant concentration, and solvent type were studied.

EXPERIMENTAL

Tri-*n*-octylamine (TOA) was a product of the Aldrich Chemical Company. Benzene, toluene, and chloroform were of analytical grade. Synthetic monocalcium phosphate/phosphoric acid mixture was obtained by dissolving 30 calcium oxide in a known concentration of phosphoric acid with gentle heating followed by dilution with deionized water to 1 L to make the solution composition 4 M H_3PO_4, 8.1 g/L Ca^{+2} at pH 2.2. The synthetic solution had the same chemical composition as the leachate solution obtained from phosphoric acid leaching of a sample of "Abu-Tartur" phosphate ore (13).

PROCEDURE

Uranyl nitrate solution was added to the synthetic MCP/H_3PO_4 aqueous solution to make it 3.36×10^{-5} M in uranium. Then the solution was treated with a few drops of a 0.01 N $KMnO_4$ solution (until a faint color appeared) to keep the uranium in the VI state and to destroy the organic matter as in the actual leachate solution. This solution was made to a known concentration with the counteranion under investigation. The counteranions used were oxalate (0.001–0.012 M), citrate, and trichloroacetate (0.01–0.2 M). TOA was diluted with the solvent under consideration and pre-equilibrated with an equal volume of 0.01 M solution of the counteranion under investigation to provide the extractant solvent that will effectively extract the required species by the active constituent of the solvent.

Equal volumes (5 mL) of the aqueous and the preequilibrated organic phases were shaken for 10 minutes in a thermostated shaker water bath at 25°C. This time was enough for equilibrium to take place. Separation of the two phases was done by centrifugation, and the uranium concentration was determined in the organic layer by stripping it with an equal volume of an aqueous solution of 0.25% arsenazo(III) in 6 M nitric acid (prepared from the concentrated acid presaturated with urea). The absorbance was measured at 655 nm (14) on a Shimadzu-160 A double beam spectrophotometer.

The distribution ratio D is defined as

$$D = \frac{C_{\mathrm{U\ org}}}{C_{\mathrm{U\ aq}}} = \frac{C_{\mathrm{U\ total}} - C_{\mathrm{U\ aq}}}{C_{\mathrm{U\ aq}}}$$

and the extraction efficiency E is defined as

$$E = \frac{D}{D + V_{\mathrm{aq}}/V_{\mathrm{org}}} = \frac{C_{\mathrm{U\ total}} - C_{\mathrm{U\ aq}}}{C_{\mathrm{U\ total}}}$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively, and C represents the concentration of uranium.

RESULTS AND DISCUSSION

Figures 1–3 give the extraction efficiency of uranium as anionic complexes by 10% TOA dissolved in benzene, toluene, and chloroform as a function of the complexing anion (oxalate, citrate, and chloroacetate) concentrations. The highest extraction occurred in the presence of oxalate anions. This may be explained by the stable uranium–oxalato anionic complexes formed ($pk_{a1} = 1.19$; equilibrium constant for the proton transfer reaction of oxalic acid), that can be extracted by TOA solution in the organic phase. At the solution acidity used, it is not expected that citric acid can form anionic species that may complex with uranyl ions ($pk_{a1} =$

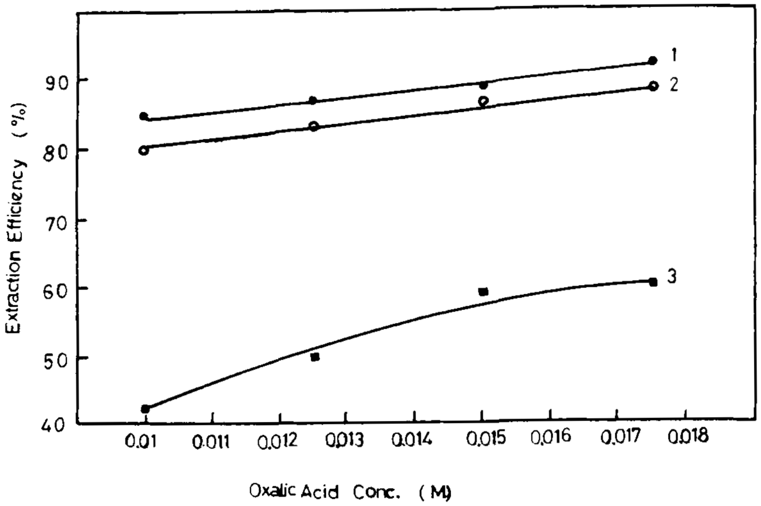

FIG. 1 Effect of oxalic acid concentration in MCP/H_3PO_4 solution on the extraction efficiency of uranyl ions by 10% TOA in different solvents: (1) benzene, (2) toluene, (3) chloroform.

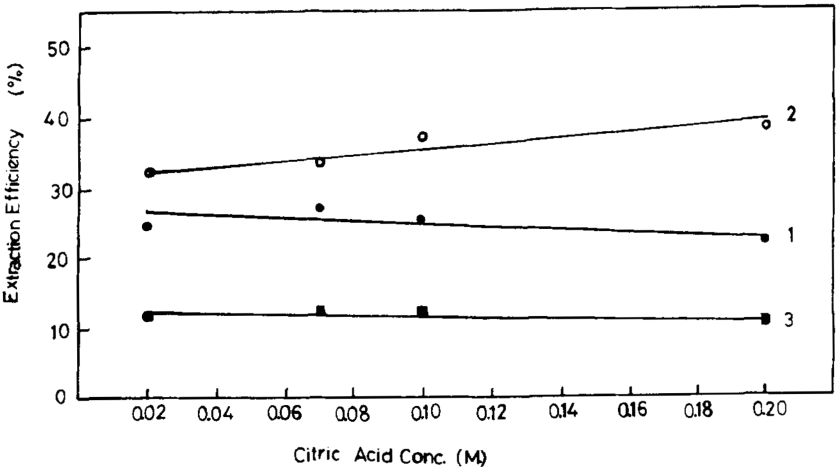

FIG. 2 Effect of citric acid concentration in MCP/H_3PO_4 solution on the extraction efficiency of uranyl ions by 10% TOA in different solvents: (1) benzene, (2) toluene, (3) chloroform.

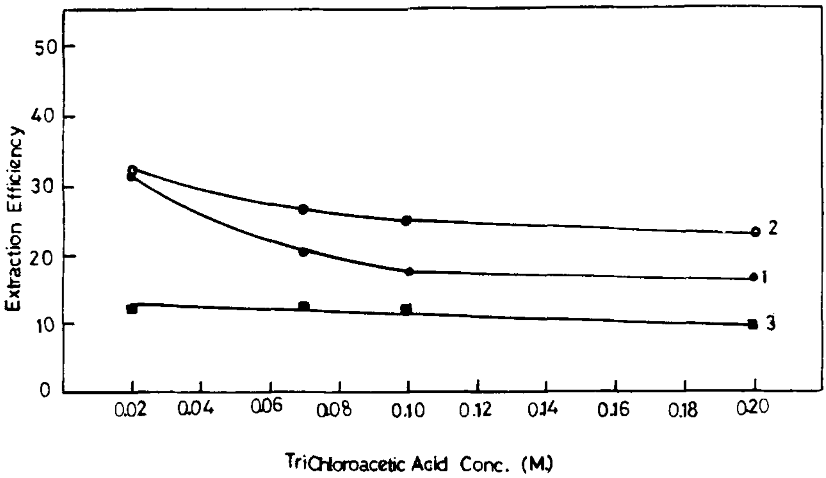

FIG. 3 Effect of trichloroacetic acid concentration in MCP/H_3PO_4 solution on the extraction efficiency of uranyl ions by 10% TOA in different solvents: (1) benzene, (2) toluene, (3) chloroform.

3.13) (15). In the case of trichloroacetic acid (pk_{a1} = 0.64), the complex formed with uranyl ions is too weak (16) and hence doesn't enhance the extraction.

The discussion of stability constants (log β) for metal complexes MA_n (M = metal ion, A_n = carboxylate ligands) is also applicable to the stability of the acid, HA. Thus, large log β_n values are usually observed for organic acid with a large pk_a, and hence a high extraction constant is directly proportional to the large log β and pk_a values needed to obtain the high concentration of free ligands which favors the formation of the MA_n complexes. The anions of dicarboxylic acid, and even more those of polycarboxylic acids, generally appear to have a stronger tendency for complex ion formation with uranyl ions (17). This can be represented as

$$UO_2^{2+} + nA \leftrightharpoons UO_2A_n^{2-n}$$

where A^- is the complexing onion and n is its coordinated number. TOA may be equilibrated through contact with a low concentration of organic acid:

$$R_3N_{(org)} + HA_{(aq)} \leftrightharpoons R_3NH^+A^-_{(org)}$$

where R_3N is the tertiary amine TOA.

In practice the anion of the equilibrated amine is usually the same as that which complexes M^{z+}, For example:

$$R_3NH^+A_{(org)} + MA^-_{n(aq)} \leftrightarrows R_3NH^+MA^-_{n(org)} + A^-_{(ag)}$$

where MA_n^- represent the uranium–carboxylate anionic complex. The ion pairs formed are hydrophobic and highly soluble in organic solvents. This reaction is an anion-exchange process.

From the data obtained it is seen that the extraction efficiency of TOA is greater if it is dissolved in benzene or toluene than in chloroform. The latter solvent forms hydrogen bonds with the organic extractant (18) and hence lowers the percent uptake of the uranium–carboxylate complex which dissociates in highly polar solvents.

Figure 1 also shows that the uptake of the uranium anion complex is increased by the addition of excess oxalic acid which is at a maximum at an acid concentration of 0.015 M. Any further increase of the oxalic acid causes precipitation of calcium oxalate.

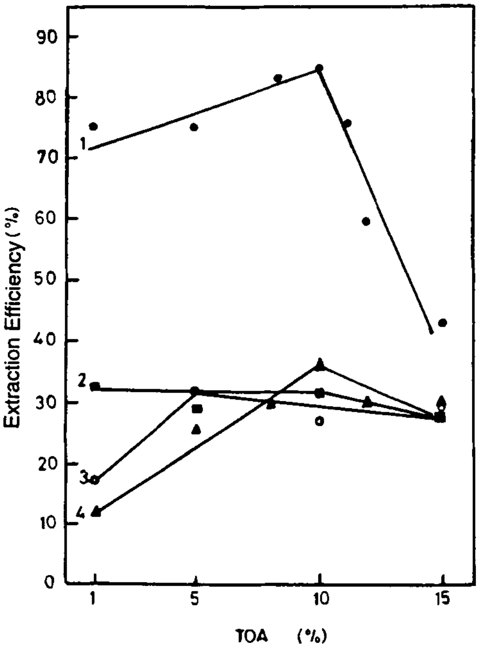

FIG. 4 Effect of volume percent of TOA on the extraction efficiency of uranyl ions between benzene and MCP/H_3PO_4 solution in carboxylic acid solution: (1) oxalic acid, 0.01 M; (2) trichloroactic acid, 0.02 M; (3) citric acid, 0.07 M; (4) no carboxylic acid.

Increases of citric or trichloroacetice acid concentrations were not expecting to vary the uptake of uranium from the MCP/H_3PO_4 aqueous solution due to the weak dissociation of the first and the instability of the complex formed by the latter. This is indicated in Figs. 2 and 3.

It is worth noting that the extraction efficiency of uranyl ion by tri-*n*-octylamine in the absence of any counteranions, which was 36%, increased to almost 90% in the presence of 0.01 M oxalic acid. This can be explained by interaction at the molecular scale or by the salting out effect of the calcium ions that will orient the dipole of a polar solvent by its electrical charge because donor–acceptor bonds may be formed in the solute and solvent. The Ca^{2+} and $TOAH^+UO_2A_n^-$ ion-pair have suitable electron pair donation and acceptance properties.

Data in Fig. 4 show that the uranium extraction efficiency reaches a maximum at 10% TOA and then decreases as the volume percent of TOA is increased. This is a typical behavior of TOA which dimerizes at high concentrations as follows (18):

$$2R_3NH^+A^- \leftrightharpoons (R_3NHA)_2$$

Hydrogen bonding occurring between solute particles also leads to aggregation when a molecule of the solute contains both a hydrogen atom bonded to an electronegative atom (H^+ and the nitrogen atom in TOA) and another such atom or species (A^- or $MA^-{}_n$) that can accept a hydrogen bond. Larger aggregates are formed at higher amine concentrations. It is remarkable that these aggregates seem to behave like monofunctional species, each extracting only one anionic metal complex.

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