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Mojtaba Shamsipur[a]; Reza Davarkhah[b]; Yadollah Yamini[b]; Rahim Hassani[b]; Ali Reza Khanchi[c]
[a] Department of Chemistry, Razi University, Kermanshah, Iran [b] Department of Chemistry, Tarbiat Modares University, Tehran, Iran [c] Chemistry Research Department, Nuclear Science Research School, Nuclear Science and Technology Research Institute, Tehran, Iran

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# Selective Facilitated Transport of Uranium(VI) Across a Bulk Liquid Membrane Containing Benzoyltrifluoroacetone as Extractant-Carrier

**Mojtaba Shamsipur,[1] Reza Davarkhah,[2] Yadollah Yamini,[2] Rahim Hassani,[2] and Ali Reza Khanchi[3]**
[1]Department of Chemistry, Razi University, Kermanshah, Iran
[2]Department of Chemistry, Tarbiat Modares University, Tehran, Iran
[3]Chemistry Research Department, Nuclear Science Research School, Nuclear Science and Technology Research Institute, Tehran, Iran

**Abstract:** A study has been made on carrier-mediated transport of uranium(VI) using a bulk liquid membrane prepared by dissolving benzoyltrifluoroacetone (HBTA) in carbon tetrachloride. The source phase comprised of a solution of $UO_2^{2+}$ or its binary mixture with other cations such as $Th^{4+}$, $Hf^{4+}$, $Zr^{4+}$, $Fe^{3+}$, $La^{3+}$, $Cu^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Ni^{2+}$, and $Zn^{2+}$ in aqueous solutions of pH 6.0, while 0.1 M hydrochloric acid was serving as a stripping agent in the receiving compartment. The interference from $Th^{4+}$ and a few other cations could be eliminated by using trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (DCTA) as a proper masking agent in the feed solution. Various factors influencing the transport process have been studied and an uphill transport (>99%) of uranium(VI) from the source phase could be accomplished under optimum conditions.

**Keywords:** Benzoyltrifluroacetone, bulk liquid membrane, uphill transport, Uranyl ions

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Address correspondence to Mojtaba Shamsipur, Department of Chemistry, Razi University, Kermanshah, Islamic Republic of Iran. Fax: +98 21 66908030. E-mail: mshamsipur@yahoo.com

## INTRODUCTION

The use of various types of liquid membranes for separation processes has been increasing in recent years. Membrane technology has been widely utilized for carrier mediated metal ion separations (1–5) and, to a lesser extent, for the separation of organic substances (6–8). The principle of such separation techniques was described by Danesi et al. (9). An important advantage for the use of such techniques is that in the liquid membrane technology the extraction, stripping, and regeneration operations are combined in one single step. The facilitated or carrier-mediated transport of metal ions across liquid membranes has received increased attention of many chemists due to its applications in various fields such as nuclear industries, particularly for the separation and purification of uranium from low level concentration sources (10). In this kind of transport, the utility of the system for separation of metal ions will be governed by the choice of carrier molecule added to the membrane phase (11).

Acidic ligands are frequently used as extractant-carriers for separation of metal ions in proton-driven cation transport systems (12–14). In such transport systems, the uphill transport against a cation concentration gradient is feasible since the cations are transferred by countertransport of protons. ß-Diketones are well known as useful chelating agents in analytical chemistry, chelate chemistry, and radiochemistry, and due to their acidic properties, they have been utilized for the proton-driven transport of actinides (15,16).

Because uranium is a relatively mobile element in many surface or near-surface environments, its geochemical exploration methods require the measurement of the trace quantities of the metal ion in water samples (17,18), along with that in plants, soils, and rocks. The uranium concentration of seawaters is about 3.3 μg $L^{-1}$ (19), in freshwaters even lower. Thus, highly sensitive methods are required for the separation, preconcentration, and determination of water samples collected for prospecting purposes. It should be noted that uranium is a chemical toxin as well as being radioactive; the safety profiles for uranium compounds are well established (20). Uranium monitoring in all process streams of fuel-pellet preparation and in radioactive waste is also of critical importance (21). In the past decade, we have been involved in the solid phase extraction (22–24), supercritical fluid $CO_2$ extraction (25), and preparation of optical (26) and potentiometric sensors for uranyl ions (27–29).

In the present paper, we were interested in studying the ability of benzoyltrifluoroacetone (HBTA) as a mobile carrier for the selective separation of uranium(VI) ions from aqueous media using a bulk liquid membrane system. It is noteworthy that this ligand is well known as an extracting agent for metal ions alone, or via its combination with other extractants in synergistic solvent extraction experiments (30–32). Thus, the influences of various experimental parameters, which may affect the transport behavior of uranium, viz. nature of diluent, carrier concentration, feed acidity, and the type and concentration of the acid used as stripping agent in the receiving phase have been investigated. The carrier activity of HBTA towards the selective transport of uranium in the presence of thorium and several other interfering ions has also been studied.

## EXPERIMENTAL

### Reagents

Reagent grade benzoyltrifluoroacetone (HBTA) and trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid hydrate (DCTA) were obtained from Aldrich and used without further purification. Carbon tetrachloride, dichloromethane, chloroform, 1,2-dichloroethane, and the acids used were purchased from Merck chemical company and used as received. A stock solution of 0.01 M ($1\,M = 1\,mol\ dm^{-3}$) uranium was prepared from $UO_2(NO_3)_2.6H_2O$ (Merck). The $Th^{4+}$, $Hf^{4+}$, $Zr^{4+}$, $Fe^{3+}$, $La^{3+}$, $Cu^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Ni^{2+}$ and $Zn^{2+}$ solutions were prepared from the corresponding reagent grade nitrate salts (Merck or Fluka). Doubly distilled water was used throughout.

### Apparatus

All measurements were performed with a simultaneous inductively coupled plasma-atomic emission spectrometer (ICP-AES, Varian Vista-Pro, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD). The ICP conditions used are shown in Table 1. The pH of solutions was adjusted using a model 620 Metrohm pH meter with a combined glass-calomel electrode.

### Procedure

All transport experiments were carried out at the ambient temperature of 23 ± 1°C. A cylindrical glass cell (inside diameter 4.0 cm) holding a glass tube (inside diameter 2.0 cm), thus separating the two source and receiving aqueous phases was used. A schematic representation of the BLM cell used has already been reported by Akhond and Shamsipur (33). The inner aqueous phase (source phase, SP) contained U(VI) or a binary mixture of metal ions at a fixed pH of 6.0 (5 mL). The outer aqueous

**Table 1.** Instrumental and operating conditions ICP-AES measurements

| Parameter | Type or amount |
|---|---|
| Frequency generator (MHz) | 40 |
| Plasma viewing mode | Radial |
| Viewing height (mm) | 8 |
| Injector i.d. (mm) | 2.5 |
| Optical mount | Echelle grating + cross-dispersion |
| Grating line number ($mm^{-1}$) | 95 |
| Focal length (cm) | 40 |
| Detector | CCD |
| Nebulizer | Concentric |
| Spray Chamber | Cyclonic |
| RF Power (kW) | 1.2 |
| Plasma gas flow rate ($l\ m^{-1}$) | 13.5 |
| Auxilary gas flow rate ($l\ m^{-1}$) | 0.75 |
| Nebulizer pressure (KPa) | 200 |
| Rinse time (s) | 10 |
| Selected emission line (nm) | U (367.007) |

phase (receiving phase, RP) contained 0.1 M hydrochloric acid (10 mL). The carbon tetrachloride membrane phase (MP, 20 mL) containing $1.0 \times 10^{-4}$ M HBTA lay below these aqueous phase, and bridged the two aqueous phases. The organic layer was magnetically stirred by a Teflon-coated magnetic bar (3 cm × 5 mm diameter). Samples of both aqueous phases were analyzed for metal content by inductively coupled plasma-atomic emission spectrometry (ICP-AES). A similar transport experiment was carried out in the absence of the carrier for reference. Detailed conditions of experiments carried out in order to obtain optimal conditions are included in tables and figures.

The reproducibility of the above system was investigated by accomplishing five replicate transport experiments. The percent of metal ion transported in to the receiving phase after 6 h was found to be $(99.5 \pm 1.7)\%$.

## RESULTS AND DISCUSSION

### Transport Mechanism

The mechanism of the transport of U(VI) across the bulk liquid membrane (BLM) is schematically represented in Fig. 1. HBTA is a ß-diketone and, in its enolic form, it has a replaceable hydrogen atom and thus is shown as HR in the figure. At the source phase/membrane

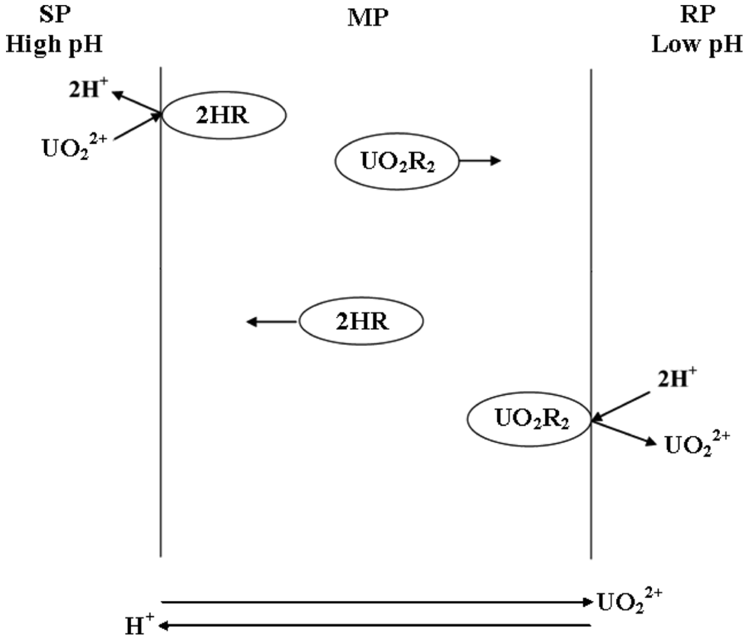

*Figure 1.* Simplified representation of the uphill transport of U(VI) ion across bulk liquid membrane.

interface, the U(VI) ions are absorbed into the membrane due to strong complex formation with HBTA. At this stage, the carrier gives up protons into the feed phase as a result of complex formation with uranyl ion. The neutral uranyl-carrier complex thus formed diffuses down its concentration gradient. On the other side of the membrane, the U(VI) ion is released into the aqueous receiving phase due to stripping action of the $H^+$ ion. The free protonated carrier then diffuses back across the membrane to the feed phase/membrane interface and the cycle will be repeated. The concentration polarization of different species was minimized by continuous and uniform stirring throughout the experiment. The net result is the transport of uranium(VI) from the aqueous source phase into the aqueous receiving phase across the bulk of the organic phase, at the expense of countertransport of equivalent amounts of protons.

## Effect of pH of Source Phase

Since the carrier HBTA is an acidic ligand, its extractive mobile carrier properties are expected to be dependent on pH of feed solution. In order

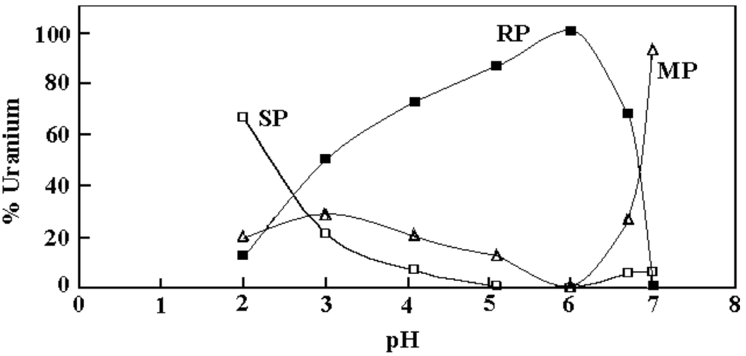

*Figure 2.* Effect of pH of source phase on the transport of uranium(VI): Conditions: source phase, 5 mL of $1.0 \times 10^{-4}$ M U(VI) at pH 6.0; membrane phase, 20 mL of 0.02 M HBTA in carbon tetrachloride; receiving phase, 10 mL of 0.1 M hydrochloric acid; time of transport, 6 h.

to study the effect of hydrogen ion concentration, the transport experiments of uranium ions (initial concentration $1.0 \times 10^{-4}$ M) from aqueous medium through carbon tetrachloride membrane containing HBTA (0.02 M), into a hydrochloric acid solution (0.1 M) as a function of pH of the feed phase in the range of 2.0–7.0 were carried out (Fig. 2).

The results show an augmentation in the transport of uranium ions from the source phase into the membrane and its release into the receiving phase by increasing pH of the source phase. As is obvious from Fig. 2, the quantitative transport of uranyl ion into the receiving phase occurs at an optimum pH of 6.0, with no measurable uranyl ion remaining in the source and membrane phases. However, at lower and, especially, higher pH values, the uranium transport will diminish drastically. The decreased transport of uranyl ion into the receiving phase at lower pH values can be mainly related to the increased competition of proton with uranyl ion for the carrier HBTA in membrane phase.

While as is obvious from Fig. 2, after 6 h transport at a source phase pH of 7.0, the uranyl content of both the aqueous source and strip phases found to be close to zero, as determined by ICP-AES. Consequently, almost all uranyl ions should be either in the membrane phase or, more possibly, precipitated in their water insoluble hydroxide forms at the source phase/membrane interface (34). Thus, in order to check the presence of uranyl ion in the membrane phase, an aliquot of membrane phase was evaporated and the residue was dissolved in butyl propionate and the uranium content was measured spectrophotometrically using the method proposed by March (32). As expected at a pH of 7 (35), the uranyl content of the membrane phase was found to be negligible. Thus, the precipitation of uranyl hydroxide at the source phase/membrane phase interface seems to be the most possible reason for the diminished transport ability of the system at pH 7.0 and higher.

## Effect of HBTA Concentration in the Organic Phase

The influence of the carrier concentration in the organic phase on the transport efficiency of uranium was studied and the results are shown in Fig. 3. As seen, while no measurable transport occurs in the absence of a carrier, an increase in HBTA concentration in the organic phase from 0 to 0.02 M leads to an increase in uranyl transport. Meanwhile, a further increase in HBTA concentration in organic phase from 0.02 to 0.12 will result in a slight decrease in uranyl transport. This is despite the fact that, from the kinetic point of view, it is desirable to work at higher carrier concentrations.

Thus, in order to obtain further information about the kinetic aspects of uranyl transport, the apparent rate constant of uranium transport, $k_{obs}$ ($s^{-1}$), at various concentrations of HBTA was evaluated from the slope of the linear plot of $\ln([U]_{s,t}/[U]_{s,0})$ against time t based on equation $\ln([U]_{f,t}/[U]_{f,0}) = k_{obs}.t$ (36), where $[U]_{s,0}$ and $[U]_{s,t}$ are the source phase initial uranium concentration and uranium concentration at time t, respectively. The resulting plot of influence of HTBA concentration on the $k_{obs}$ is shown in Fig. 4. As it is seen from Fig. 4, the apparent rate constant of uranium transport, $k_{obs}$, was found to gradually increase with

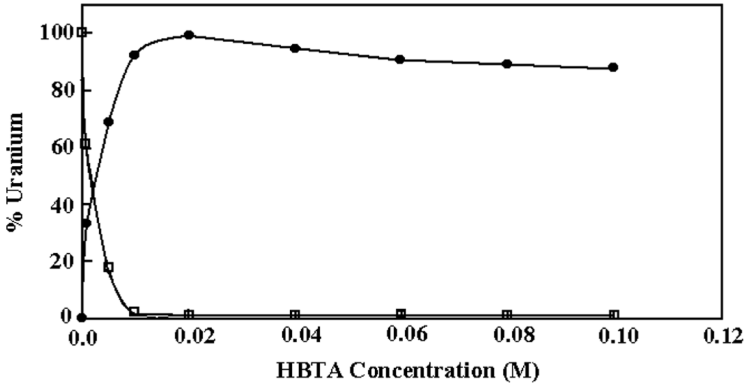

*Figure 3.* Effect of HBTA concentration in the membrane phase on uranium transport: (●) receiving phase; (☐) source phase. Conditions: source phase, 5 mL of $1.0 \times 10^{-4}$ M U(VI) at pH 6.0; membrane phase, 20 mL of varying concentration of HBTA in carbon tetrachloride; receiving phase, 10 mL of 0.1 M hydrochloric acid; time of transport, 6 h.

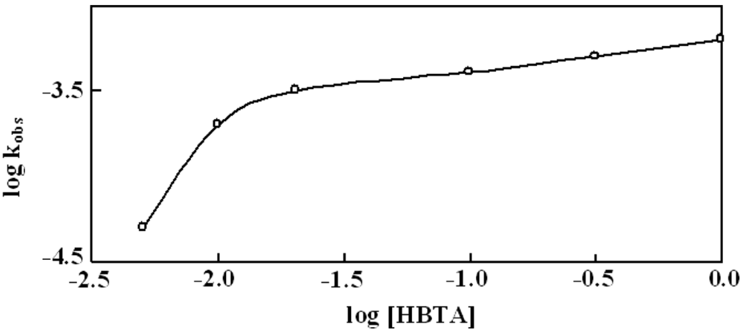

***Figure 4.*** Effect of carrier concentrations on $k_{obs}$. Conditions: source phase, 5 mL of $1.0 \times 10^{-4}$ M U(VI) at pH 6.0; membrane phase, 20 mL of 0.02 M HBTA in $CCl_4$; receiving phase, 10 mL of HCl solution; time of transport, 6 h.

increasing HBTA concentration from $3.0 \times 10^{-4}$ $s^{-1}$ (at 0.02 M) to $4.0 \times 10^{-4}$ $s^{-1}$ (at 0.1 M). It seems reasonable to assume that HBTA concentrations greater than 0.02 M do not favor the release of metal ion into the receiving phase in spite of increasing transport rate, as reported before (11). The above observations suggest that HBTA has a definite carrier activity toward transport of uranium. Thus, in all subsequent experiments, the carrier concentration was maintained at 0.02 M.

## Effect of the Nature of Organic Membrane

The influence of the diluent type in the membrane on the transport efficiency was also studied. The results showed that, under the same experimental conditions, the percentage transport of uranium ions into the receiving phase decreased in the order $CCl_4$ (99.5%) > $CH_2Cl_2$ (79.2%) > $C_2H_4Cl_2$ (70.0%) > $CHCl_3$ (67.6%). The polarity of the organic diluent as well as the viscosity and other physical properties of diluents are known to influence the efficiencies of an extractant-carrier system in a membrane (37). Thus, the behavior observed in the present investigation may be attributed to a combination of variety of physical properties which simultaneously affect the transport phenomenon.

## Effect of the Nature and Concentration of the Mineral Acid in Receiving Phase

The nature and composition of the receiving phase was found to have a dramatic influence on the transport efficiency. Because the carrier in this study is an acidic ligand, it is necessary to maintain the hydrogen-ion

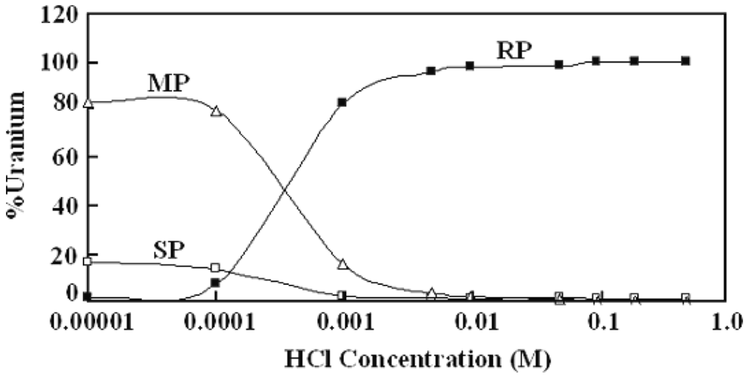

***Figure 5.*** Effect of HCl concentration in receiving phase on uranium(VI) transport. Conditions: source phase, 5 mL of $1.0 \times 10^{-4}$ M U(VI) at pH 6.0; membrane phase, 20 mL of 0.02 M HBTA in $CCl_4$; receiving phase, 10 mL of HCl solution; time of transport, 6 h.

concentration gradient between both sides of the membrane, in order to move uranium across the membrane. Therefore, the selection of a suitable mineral acid in receiving phase is required for the stripping process. The order of the percentage of uranium ions transported into the receiving phase with the application of 1 M concentration of four different acids (i.e., hydrochloric, nitric, sulfuric, and perchloric acids) was found to vary as follows: HCl (99.5%) $> HClO_4$ (88.6%) $> H_2SO_4$ (80.9%) $> HNO_3$ (77.8%). It seems that the tendency of chloride ion is highest among the series used for the stripping of uranium, via formation of stable $UO_2Cl_4^{2-}$ species (38), from the membrane into the receiving phase, as reported before (13,39).

The effect of the variation in the concentration of hydrochloric acid on the transport of uranium was also studied and the results are summarized in Fig. 5. As is obvious, the percentage transport of uranyl ion increases with increasing concentration of hydrochloric acid until a 0.1 M acid solution is added. However, further addition of acid into the receiving phase shows no significant increase in uranium transport. Thus, a solution of 0.1 M of hydrochloric acid was used as receiving phase in all experiments.

## Effect of Transport Time

The variation of uranium concentration in the feed and the receiving solutions as a function of time is shown in Fig. 6. It is obvious that the

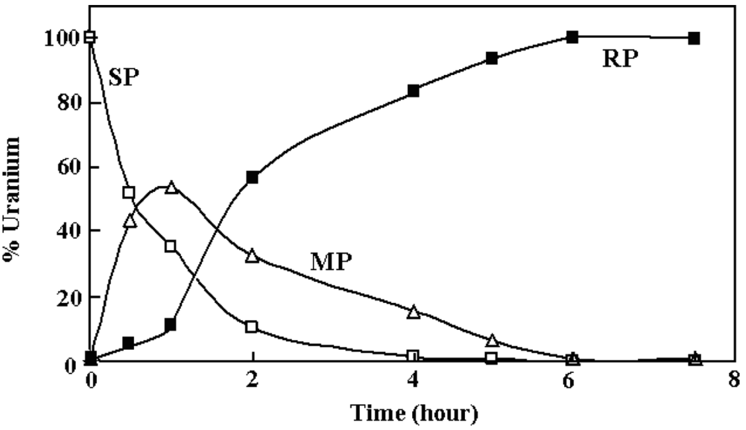

*Figure 6.* Time dependence of uranium(VI) transport. Conditions: similar to those mentioned in Table 2.

extraction of uranium from the source phase into the organic membrane occurs almost completely after 4 h. However, the release of uranium ion from the membrane phase into the receiving phase occurs at a slower rate. Thus, it seems reasonable to assume that the release uranium ion from its complex with HBTA is the rate determining of the membrane transport (40). It was found that, under the optimum conditions, the transport of uranium ion from the aqueous source phase into the receiving phase after 6 h is almost quantitative.

## Selectivity of the BLM System for Uranium(VI) Transport

In Table 2 are listed the percentage transport of uranium(VI) and $M^{n+}$ cations (i.e., $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$, $La^{3+}$, $Hf^{4+}$, $Zr^{4+}$, $Th^{4+}$) which were present with uranyl ion in equimolar concentrations, into the receiving phase. As it is obvious from Table 2, in the absence of a masking agent in the source phase, while the interfering effects of some metal ions including $Mn^{2+}$, $Hf^{4+}$ and $Zr^{4+}$ is negligible (from 0.7% to 4.2%) other cations tested show intermediate (i.e, $Co^{2+}$ 18.5%, $Th^{4+}$ 20.7%, and $Fe^{3+}$ 28.5%) and high (i.e., $Ni^{2+}$ 32.9%, $La^{3+}$ 46.1%, $Cu^{2+}$ 70.2%, and $Zn^{2+}$ 82.9%) interfering effects. This is because HBTA is a well-known versatile chelating agent for a variety of metal ions. Thus, it was necessary to add a suitable masking agent like trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid hydrate (DCTA) to eliminate the interference effects of these ions during selective transport of uranium from aqueous media (41).

**Table 2.** Amount of uranyl ion transported from various cation mixtures through the membrane[a]

| No. | Mixture | % Transported into stripping phase | % Remaining in source phase | % Remaining in membrane phase |
|---|---|---|---|---|
| I | $UO_2^{2+}$ | 95.9 | 1.9 | 2.2 |
| | $Th^{4+}$ | 20.7 | 6.4 | 72.9 |
| II | $UO_2^{2+b}$ | 84.5 | 15.5 | 0.0 |
| | $Th^{4+}$ | 2.5 | 78.4 | 19.1 |
| III | $UO_2^{2+}$ | 98.5 | 0.0 | 1.5 |
| | $Fe^{3+}$ | 28.5 | 1.5 | 70.0 |
| IV | $UO_2^{2+b}$ | 99.9 | 0.1 | 0.0 |
| | $Fe^{3+}$ | 16.1 | 73.1 | 10.8 |
| V | $UO_2^{2+c}$ | 97.8 | 0.3 | 1.9 |
| | $Fe^{3+}$ | 12.9 | 87.1 | 0.0 |
| VI | $UO_2^{2+d}$ | 86.1 | 5.5 | 8.4 |
| | $Fe^{3+}$ | 12.9 | 87.1 | 0.0 |
| VII | $UO_2^{2+}$ | 90.7 | 0.0 | 9.3 |
| | $Cu^{2+}$ | 70.2 | 2.1 | 21.7 |
| XIII | $UO_2^{2+b}$ | 99.1 | 0.0 | 0.9 |
| | $Cu^{2+}$ | 2.6 | 81.3 | 16.1 |
| IX | $UO_2^{2+}$ | 99.5 | 0.0 | 0.5 |
| | $Co^{2+}$ | 18.5 | 50.3 | 31.2 |
| X | $UO_2^{2+b}$ | 96.9 | 0.0 | 3.1 |
| | $Co^{2+}$ | 0.0 | 68.6 | 31.4 |
| XI | $UO_2^{2+}$ | 90.5 | 0.0 | 9.5 |
| | $Mn^{2+}$ | 0.7 | 73.4 | 25.9 |
| XII | $UO_2^{2+b}$ | 96.9 | 0.0 | 3.1 |
| | $Mn^{2+}$ | 0.2 | 75.4 | 24.4 |
| XIII | $UO_2^{2+}$ | 95.5 | 0.0 | 4.5 |
| | $Zn^{2+}$ | 82.9 | 7.1 | 10.0 |
| XIV | $UO_2^{2+b}$ | 98.7 | 0.0 | 1.3 |
| | $Zn^{2+}$ | 7.9 | 92.0 | 0.1 |
| XV | $UO_2^{2+}$ | 84.8 | 0.3 | 14.9 |
| | $Ni^{2+}$ | 39.2 | 26.4 | 34.4 |
| XVI | $UO_2^{2+b}$ | 88.1 | 0.6 | 11.3 |
| | $Ni^{2+b}$ | 2.3 | 64.9 | 32.8 |
| XVII | $UO_2^{2+}$ | 75.1 | 0.0 | 24.9 |
| | $Hf^{4+}$ | 3.8 | 0.7 | 95.5 |
| XIII | $UO_2^{2+b}$ | 81.4 | 0.1 | 18.5 |
| | $Hf^{4+}$ | 1.1 | 98.9 | 0.0 |
| XIX | $UO_2^{2+}$ | 86.8 | 0.0 | 13.2 |
| | $La^{3+}$ | 46.1 | 17.6 | 36.3 |

(*Continued*)

**Table 2.** Continued

| No. | Mixture | % Transported into stripping phase | % Remaining in source phase | % Remaining in membrane phase |
|---|---|---|---|---|
| XX | $UO_2^{2+b}$ | 81.3 | 0.0 | 18.7 |
| | $La^{3+}$ | 0.0 | 99.3 | 0.7 |
| XXI | $UO_2^{2+}$ | 91.5 | 0.5 | 8.0 |
| | $Zr^{4+}$ | 4.2 | 17.2 | 78.6 |
| XXII | $UO_2^{2+b}$ | 87.8 | 0.1 | 12.1 |
| | $Zr^{4+}$ | 0.9 | 99.1 | 0.0 |

[a]Conditions: source phase, 5 mL of $1.0 \times 10^{-4}$ M of each cation in the binary mixture at pH 6.0; membrane phase, 20 mL of 0.02 M HBTA in $CCl_4$; receiving phase, 10 mL of HCl; time of transport 6 h.

[b]In the presence of 0.01 M DCTA.

[c]In the presence of 0.01 M DCTA + 0.001 M $F^-$.

[d]In the presence of 0.01 M DCTA + 0.01 M $F^-$.

Thus, in the next step, the selectivity of uranium transport in the presence of other metal ions was studied in the presence of 0.01 M DCTA, at pH 6.0, as a potential masking agent in the feed solution. The results of these series of transport experiments are also included are in Table 2. As it is seen from Table 2, in the presence of DCTA, the transport of eight of ten interfering metal ions (i.e., $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $La^{3+}$, $Hf^{4+}$, $Zr^{4+}$, $Th^{4+}$) were considerably diminished to 0.0 to 2.6% in the expense of some decrease in the percent transport of uranyl ion, while the percentage of $Zn^{2+}$ and $Fe^{3+}$ ions transported decreases to final values of 7.9% and 16.1%, respectively. The use of another masking agent like fluoride ion together with DCTA (0.01 M of each) resulted in a further decrease in transport of $Fe^{3+}$ ion from 16.1% to 12.9%.

The resulting selective transport of uranium in the presence of thorium and transition metal ions and DCTA is understandable from a consideration of the stability constants of their DCTA complexes. The logarithm of the stability constant for DCTA-uranium(VI) complex is 5.27, the corresponding values for $Th^{4+}$, $Cu^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Fe^{3+}$, $Zr^{4+}$ and $La^{3+}$ complexes with DCTA are 23.2, 21.3, 18.9, 16.8, 19.4, 18.7, 29.3, 29.9, and 16.3, respectively (42–44). Thus, the concentration of free uranium will be reasonably high due to the relatively low stability of its complex with DCTA, while that of the other metal ions is expected to be too low to compete effectively with the transport of uranyl ion. Moreover, the DCTA complexes of all the interfering ions are anionic and highly hydrophilic, which in turn, prevents the transport of these ions across the organic membrane as their DCTA complexes.

## CONCLUSION

Benzoyltrifluoroacetone can be successfully used as carrier for the uphill transport of uranium(VI) across a carbon tetrachloride bulk liquid membrane (BLM). For the best results, the following optimized conditions are used: pH of the feed phase, 6.0; concentration of the carrier in membrane phase, 0.02 M; concentration of hydrochloric acid in the receiving phase, 0.1 M. DCTA found to be a suitable and effective masking agent for thorium and some interfering transition metal ions so that, in the presence of 0.01 M DCTA and under optimum conditions, a quantitative and selective recovery of uranium ions is achieved. The present study may be useful for the separation of uranium(VI) ion from the leach solutions obtained from hydrometallurgical operations and treatment of nuclear materials.

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