REMOVAL OF URANYL IONS UO$_2^{2+}$
FROM DILUTE SOLUTIONS BY ELM TECHNIQUE.
I. TRANSPORT MECHANISM OF URANYL IONS
WITH AMMONIUM QUATERNARY SALTS AS CARRIER

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abstract: The separation of uranyl ions from dilute solutions can be realized by a facilitated transport using ammonium quaternary salts as carrier (Aliquat 336), dissolved in an organic membrane. This process was realized by ELM technique. By this method, aqueous solutions containing uranyl ion in the range 4–10 mg/L were extracted and concentration reduced to under 0.4 mg/L so that these solutions can be delivered to surface waters. The inverted emulsions used in extractions were obtained by stirring equal volumes of organic phase (kerosene) and aqueous stripping solution containing NaHCO$_3$ 1 M, and Span 80 as emulsifier. The extraction yields are determined by the pH of source phase, a maximum around pH = 5 being observed. The extraction yields are also determined by the emulsion / source phase ratio.

Introduction

Liquid membranes containing mobile complexing agents have been widely studied in the form of inverted emulsions known as emulsion liquid membranes (ELM). The method has been proposed for the first time by Li [1]. The present work presents the possibility of using ELM method to separate the uranyl ions UO$_2^{2+}$ from dilute solutions and waste waters.

The extraction mechanism implies the use of an ammonium salt, Aliquat 336 (trioctyl methyl ammonium chloride) as carrier, dissolved in the liquid membrane formed of kerosene. The inverted emulsion is obtained by stirring the organic phase (kerosene) containing the carrier with the receiving phase, a solution of NaHCO$_3$ 1 M in the presence of emulsifier (Span 80).

By dispersing the inverted emulsion W/O in the phase source, a liquid membrane is realized between the two phases, source and receiving solution.

Extraction of uranyl ions UO$_2^{2+}$ takes place if H$_2$SO$_4$ is added to the source phase when the uranyl sulfate anion is formed (1):

\[ \text{UO}_2^{2+} + 2 \text{SO}_4^{2-} \leftrightarrow \text{UO}_2(\text{SO}_4)_2^{2-} \] (1)
The uranyl-sulfate anion reacts at the interface with the carrier Aliquat 336 to form a complex soluble in organic phase. This complex is transported to membrane / receiving phase where a reaction with HCO$_3^-$ take place to form an insoluble in organic phase uranyl-carbonate complex UO$_2$(HCO$_3$)$_2^{2-}$ [2÷4].

The entire separation mechanism is illustrated in the following scheme:

![Chemical Reaction Diagram](image)

In this way, the concentration of uranyl-ions in receiving phase is taking place against the concentration gradient. In the same time, HCO$_3^-$ is transported in countercurrent from receiving phase to source phase.

**Materials and Methods**

The solution of uranyl ions were obtained by dissolving uranium octoxid (U$_3$O$_8$) in concentrated nitric acid and dilution with distilled water to concentration between 4÷10 mg/L.

The organic membrane was composed of kerosene (Merck) having dissolved the carrier, Aliquat 336 (Fluka) and the emulsifier (Span 80). Equals volumes of organic phase and receiving solutions (NaHCO$_3$ 1 M) were stirred using a Cole & Parmer high-speed stirrer to obtain the inverted emulsions.

The extraction of uranyl ions from dilute solutions was realized by dispersing the inverted emulsion in the source phase (at 1:15 ratio) for times between 5÷30 min.

The yield of extractions was expressed as the ratio of uranyl ions extracted to initial quantity in system.

The residual uranyl ions remained in the source solution were determined photometrically using the Arsenazo III as indicator [5].

**Results and Discussions**

The main factor that determines the yield of extraction of uranyl ions is the pH of the source phase as illustrated in Fig. 1.

The curve yield versus pH are going through a maximum at around pH = 5. The higher yield value is obtained at longer extraction times reaching a plateau. The extending extraction time over a certain value is detrimental probably to the destruction of inverted emulsions during stirring and reintroduction of receiving solution to source phase.

The extraction yields are also affected by the emulsion / source phase ratio (Fig. 2).
Fig. 1: The influence of phase source’s pH on the extraction yield.

For economical reasons, the emulsion / source phase should be as low as possible in order to reduce the costs of operations and to increase the efficiency. From Fig. 2, one can point out that an increased ratio brings some increases in the extraction yield but not very big.

Also, one can point out that an extended extraction time can become detrimental to the extraction yield. A time of 15 min is optimal.

The extraction yield is also affected by the ratio of organic phase to receiving aqueous phase in inverted emulsion as illustrated in Fig. 3.

The increase of organic phase to aqueous phase leads to a decrease in yields, the maximum yield being obtained for 1:1 ratio.
Fig. 3: The influence organic phase ratio/receiving phase on the extraction yield.

Besides the yield of extraction versus carrier and emulsifier nature as well as the characteristics of emulsion formulation, the speed of transport from source phase to receiving solution care be characterized by the flux of uranyl ion defined by:

$$\gamma_{\text{net}} = \frac{C_{\text{RP}}}{M \cdot S \cdot t} \left[ \text{mol/cm}^2 \cdot \text{s} \right]$$

(2)

where: $C_{\text{RP}}$ is the concentration of uranyl ions in the receiving phase after time $t$, $S$ – area of separation between two phases and $M$ – molecular weight of transported species.

For dispersions of inverted emulsion in source phase the mean diameter of spherical particles was $d = 0.05$ cm and the specific surfaces of 1 ml emulsion is given by:

$$S = \frac{6}{d}$$

(3)

The $C_{\text{RP}}$ after time $t$ in receiving solution is given by:

$$C_{\text{RP}} = \left( C_0 - C_i \right) \frac{V_{\text{SP}}}{V_{\text{RP}}} \left[ \text{mol/L} \right]$$

(4)

where: $C_0$ and $C_i$ are the concentration of uranyl ions in the source phase.

The net flux vs time is presented in Fig. 4.

The net flux is decreasing in time as result of diminished concentration in phase source but the value is much higher, 100 times the fluxes obtained in the SLM technique for the same system.

These data demonstrates the high efficiency of the ELM method due to higher contact area realized by dispersion of inverted emulsion.

The higher fluxes in these methods open the possibility of extension for industrial processes of separation.
Conclusion

It was demonstrated the possibility of applying the ELM technique using ammonium quaternary salts as carrier to remove the uranyl ions from dilute solution (waste waters) with high extractions yields (85÷90%) the remaining uranyl ions concentration in the source phase are located under the value admitted for surface water delivery.

The optimal formulation for inverted emulsion was established to obtain the maximum extraction yield and speed of transfer (fluxes).

REFERENCES

5. ***STAS 12849/1-90.***