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Extraction of Uranium(VI) by Di-(2-ethylhexyl)-phosphoric acid Tributyl Phosphate and Trioctyl Phosphine Oxide Gels *

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Abstract

The gel-liquid extraction of U(VI) has been studied using the equilibrium distribution method. Gels used in this study were prepared by swelling styrene divinylbenzene with di-(2-ethylhexyl)-phosphoric acid (HDEHP), tributyl phosphate, trioctyl phosphine oxide or mixtures of HDEHP and each of the other reagents. Synergistic enhancement of extraction was obtained with the latter gels and a mechanism which accounts for the observed results was proposed.

Introduction

Though the technique of liquid-liquid extraction is extensively used for laboratory and large scale separation and concentration purposes, it is frequently beset with the problem of solvent loss through emulsification and physical entrainment, especially when the extraction of metal values from ore slurries is concerned. However, this problem can be eleminated by incorporating the extractant into a solid ore gel phase. The resulting solidified or gelatinized extractant can then be directly used for the treatment of ore slurries or packed into columns and the conventional solvent extraction process is replaced by a column operation. The first trial to use solidified organic extractants may be found in the Waxco process [1] for the separation of uranium from ore slurries and leach solutions. In this process, use was made of a solidified and pelletized solution of dioctyl phosphoric acid in paraffin wax. The pellets were agitated with the slurry, recovered by screening and stripped in the molten condition.

The idea of using crosslinked polystyrene beads for the extraction of metal ions from aqueous solutions was first reported by *Hale* [2] in 1954 and was patented a year later [3]. In 1961, *Small* [4] used a column packed with a gel of styrene divinylbenzene swelled with tributyl phosphate for the separation of uranium and some other metal ions from aqueous solutions. Since the extractant was incorporated as a part of an organic gel, he termed the process gel-liquid extraction. Gel-liquid extraction markedly differs from either reversed phase partition chromatography [5, 6] or gel chromatography [7, 8]. Copolymers used in gel-liquid extraction have low crosslinkage and consequently they can retain high amounts of extractants. As a result, the obtained gels would be expected to have high capacity per unit volume. Reversed phase chromatography, on the other hand, usually involves the use of high crosslinkage copolymers which can retain extractants mechanically only and therefore the gel capacity per unit volume is usually low [11]. Accordingly, gel-liquid extraction may be useful in extraction of metal ions from a large volume of dilute aqueous solution, whereas reversed phase chromatography is useful in the chromatographic separation of metal ions [11]. Gel-liquid extraction also differs from gel chromatography since in the latter process separation depends on the sizes of molecular solutes. As far as we know, only few publications [4, 9–13] which deal with gel-liquid extraction have appeared.

As will be shown elsewhere [14], the extraction of uranium (VI) with styrene divinyl benzene-di-(2-ethylhexyl)-phosphoric acid gels is feasible. Gels with capacity > 200 mg U(VI)/g dry styrene divinylbenzene could be prepared. However, in view of the fact that in liquid-liquid extraction, neutral organophosphorus compounds operate in combination with di-(2-ethylhexyl)-phosphoric acid and other dialkyl phosphoric extractants to synergistically enhance uranium extraction [15], it was decided to investigate the effect of incorporating tributyl phosphate (TBP) or trioctyl phosphine oxide (TOPO) into di-(2-ethylhexyl)-phosphoric acid gels in an attempt to prepare gels having the following advantages: (1) permit higher uranium loadings and (2) reduce stage requirements for any process application and (3) extend application to liquors otherwise difficult to extract.

Experimental

Materials and Reagents

Styrene crosslinked with 2% divinylbenzene (SDVB) was obtained in the form of beads of 80–150 μ diameter, from Servo Feinbiochemica Heidelberg. The beads were dried at 90 °C for three hours before use in gel preparation.

Di-(2-ethylhexyl)-phosphoric acid (HDEHP) was purchased from Fluka Co. and was purified [16] by a method which primarily depends on shaking its solution in benzene with ethylene glycol.

Tributylphosphate (TBP) was provided by BDH. It was purified

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[17] by stirring with 6N HCl solution at 60 °C, for 24 h, scrubbing with sodium carbonate and heating at about 30 °C under reduced pressure to remove any butyl alcohol or water.
Trioctyl phosphine oxide (TOPO) was purchased from Eastman Co. and was used without any further purification.
Nitrobenzene (Veb Laborchemie Apolda) was purified [18] by steam distillation in presence of dilute sulphuric acid and then distilled.
A stock solution of 0.1 M uranyl nitrate in 0.05 N HNO_3 was prepared from the "Analar" salt provided by *Hopkins* and *Williams* Co. Ltd. and was standardized by the oxinate method [19].

General Procedure of Gel Preparation

Gels used in this investigation were generally prepared according to the method described by Small [4]. Dried SDVB beads were soaked for 24 h in a solution of the extractants under test in nitrobenzene at SDVB: liquid ratio of 1:4 (weight/weight). The excess liquid was removed after centrifugation. The solvent droplets adhering to the walls of the tubes were carefully absorbed by filter paper. The gel was then well washed several times with nitric acid solution of the same concentration to be used in the experiment and soaked in the nitric acid solution, before use.

General procedure of extraction

Extraction was carried out by the equilibration batch technique. The gel obtained by swelling one gram of dry SDVB with the extractants solutions was soaked, for 24 h, in 80 ml solution of 0.02 M uranyl nitrate in nitric acid of the specified concentration. Preliminary experiments have shown that the 24 h period used for equilibration was sufficient for equilibrium to be reached under all test conditions. After equilibration, the phases were separated and U(VI) in the aqueous phase was determined spectrophotometrically by the thoron method [20].

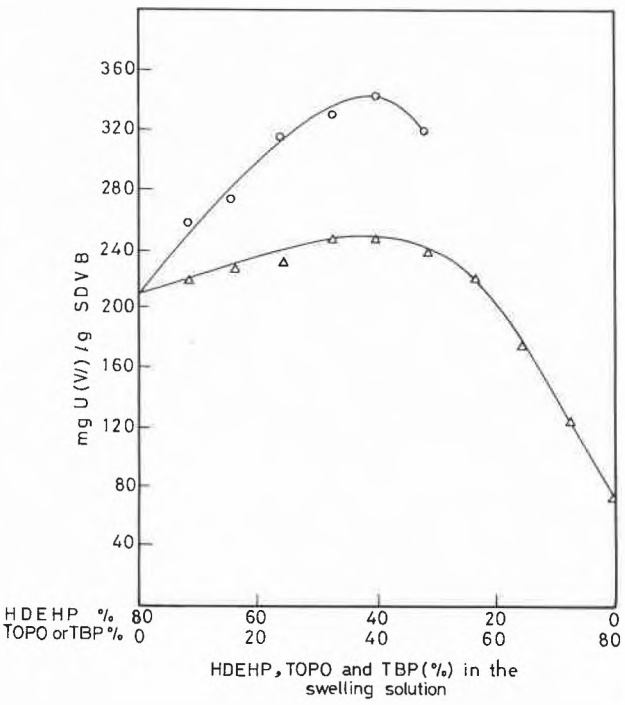


Fig. 1: Variation of gel capacity with the composition of the swelling solution.
(△) 20% nitrobenzene, 80% HDEHP + TBP in various ratios.
(○) 20% nitrobenzene, 80% HDEHP + TOPO in various ratios.

Results and Discussions

The capacities of gels prepared by swelling SDVB with solutions containing 20% by weight nitrobenzene and 80% HDEHP + TBP (or TOPO) in various weight proportions are shown in Fig. 1 which indicates that the capacity of pure HDEHP gels increases on substituting a small amount of TBP or TOPO for a similar weight of HDEHP in the swelling solution. The extent of increase of capacity depends on the organophosphorus compound/HDEHP ratio and increases as this ratio is increased to reach a maximum at a nitrobenzene : HDEHP : neutral organophosphorus extractant weight ratio of 1 : 2 : 2 and then decreases on the further increase of the fraction of organophosphorus compound in the swelling solution.
In liquid-liquid extraction of U(VI) with neutral organophosphorus compounds, N, extraction takes place according to the equation [21]:

$$UO_{2(aq)}^{++} + 2\,NO^{-}_{3(aq)} + nN \rightleftarrows UO_2(NO_3)_2 \cdot nN$$

which indicates that the amount of uranium (VI) transferred to the organic phase at equilibrium is directly proportional to the square of the aqueous nitrate ion concentration. It is to be expected that a similar mechanism is involved in the gel-liquid extraction of U(VI) with non-ionic organophosphorus gels and therefore the uranium uptake by these gels would be expected to increase with the increase of nitric acid concentration which is experimentally the case on extraction with TBP-gels at low aqueous nitric acid concentrations (Fig. 2). However, at HNO_3 concentrations greater than about 0.7 N, the uranium uptake unexpectedly decreases with the increase of acidity.

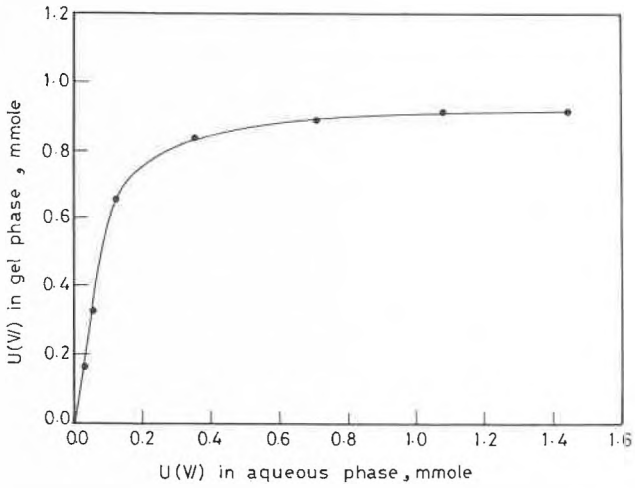


Fig. 2: Dependence of the uranium-uptake by TBP-nitrobenzene- and by TBP-HDEHP-nitrobenzene-gels on the aqueous nitric acid concentration.
TBP: nitrobenzene- (▲)1 : 4, (△) 4 : 1;
HDEHP : TBP : nitrobenzene- (●) 14 : 3 : 3, (▽) 2 : 1 : 1.

The extraction pattern obtained by TOPO-gels (Fig. 3) at low HNO_3 concentrations entirely differs from that obtained with TBP-gels. With gels of the former ex-

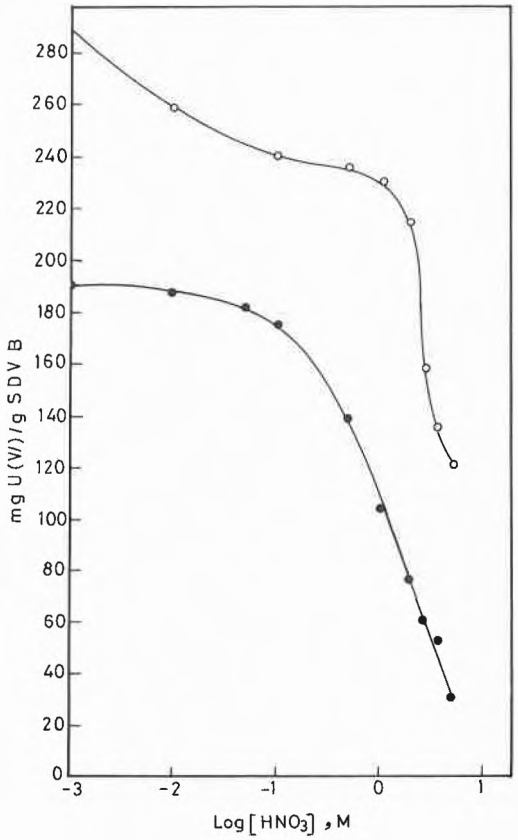


Fig. 3: Dependence of uranium extraction by TOPO-nitrobenzene- and by TOPO-HDEHP-nitrobenzene-gels on the aqueous nitric acid concentration.
(●) TOPO : nitrobenzene- 1 : 4;
(○) HDEHP : TOPO : nitrobenzene- 14 : 3 : 3.

tracant, TOPO, the uptake slightly decreases with the increase of aqueous nitric acid concentration until a maximum is reached at about 0.1 N HNO_3 and then sharply decreases. The reason of the unexpected decrease of U(VI) uptake by either TBP—(at high acidity) or TOPO—gels (at all acidities) was not investigated but since gelatinized extractants have high tendency to extract and concentrate HNO_3 [14], the decrease of the uptake of U(VI) with acidity may be due to competition between HNO_3 and $UO_2(NO_3)_2$ for the gels.

Figures 2 and 3 also show that the uptake of U(VI) by gels containing mixtures of neutral organophosphorus compounds and HDEHP is considerably greater than that of gels containing neutral organophosphorus compounds only. The removal patterns obtained with gels of HDEHP-neutral phosphorus extractants resemble those obtained with gels of only the corresponding neutral phosphorus compounds and considerably differ from the extraction patterns obtained for HDEHP-gels. With the latter gels, a cation-exchange mechanism is involved in the extraction [14] and consequently the uptake decreases with the increase of the hydrogen ion concentration.

To throw some light on the reason of the increase of the capacity of HDEHP gels when a part of HDEHP, in the swelling solution, is replaced by a neutral phosphorus extractant, the HDEHP content of HDEHP-TBP gels of the optimum capacity was determined by shaking samples of the gel with ethanol, adding distilled water to dilute the alcohol to 75% and titration against a standard alkali. The obtained results indicate that the gel contained 291.9 ± 6% mg HDEHP/g dry SDVB. To find out the saturation capacity of a gel containing such an amount of HDEHP, an isotherm for the extraction of U(VI) from 0.05 N HNO_3 solution with gels swelled with 80% solution of HDEHP in nitrobenzene was built up. The obtained results are plotted in figure 4 which shows the curve of equilibrium concentration (expressed in mmole fractions) of uranium(VI) in the gel phase versus that in the aqueous phase. Initially the curve is linear but with increasing organic-uranium concentration, the extractant is consumed, the extraction coefficient decreases and the curve levels off towards about 0.92 mmole U(VI). Since analysis indicated that the gel used in this investigation contained 1.84 mmole of HDEHP/g dry SDVB, it is deduced that at saturation one molecule of U(VI) combines with two molecules of HDEHP. Accordingly, the maximum amount of U(VI) that can be extracted by the HDEHP content (291.9 ± 6% mg/g dry SDVB) of the HDEHP-TBP gel under test is about 107.9 ± 6% mg/g dry SDVB.

Assuming that the maximum TBP content of the HDEHP-TBP-gel (prepared by soaking SDVB in a 1 : 2 : 2 mixture of nitrobenzene : HDEHP : TBP) is

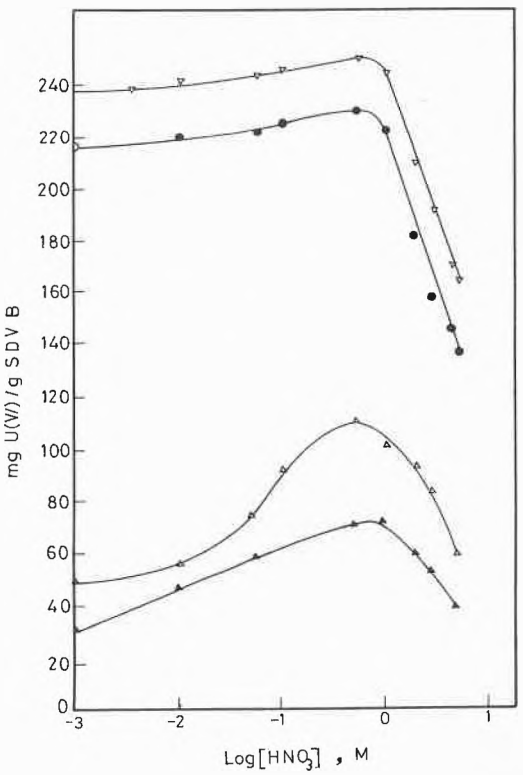
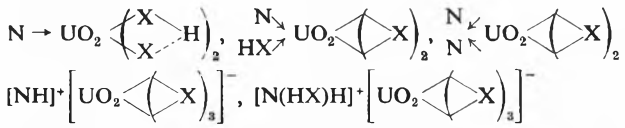


Fig. 4: Isotherm for the extraction of U(VI) by SDVB swelled with 80% solution of HDEHP in nitrobenzene.

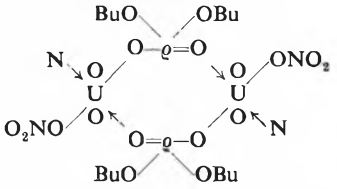
equal to that of gels prepared by soaking SDVB in 80% solution of TBP in nitrobenzene[1], the maximum U(VI) that might be extracted with the TBP amount contained in the HDEHP-TBP-gel under test would be 74.6 ± 10% mg U/g dry SDVB.[2]

From the above, it is concluded that the maximum total gel capacity would be equal to 107.9 + 74.6 = 182.5 ± 8% mg U/gram dry SDVB. Experimentally, the gel capacity for U(VI) was found to be about 247.9 ± 10% mg/g resin (i.e. the HDEHP : U(VI) molar ratio is > 2 : 1). The increase in the HDEHP-gel capacity on adding neutral organophosphorus compounds cannot therefore be attributed to a mere addition effect but may be attributed to the probable formation of mixed HDEHP-TBP-UO_2^{++} complexes. The structures proposed for such complexes and which have been postulated [22–25] to be responsible for synergism formed in the liquid-liquid extraction of UO_2^{++} with HDEHP-TBP mixture are summarized [26, 27] as follows:



(where HX = HDEHP and N = a neutral organophosphorus extractant)

As shown from the above, at U(VI) saturation, the HDEHP-gel contains HDEHP : U(VI) in the molar ratio 2 : 1. Also, all of the proposed HDEHP-TBP-UO_2 structures contain HDEHP : UO_2 in the same molar ratio, 2 : 1, or even greater. Therefore the increase in gel capacity, on the partial replacement of HDEHP with TBP, cannot be attributed to only the formation of any of the above-mentioned complexes and may therefore be due to the formation of binary species in which nitrate ions participate. For extraction of U(VI) from nitric acid by mixtures of TBP and dibutylphosphoric acid, DBP, Han and Vander Wall [28] found it essential to consider species such as $[UO_2(NO_3)_2]_2(DBP)_2$ which $(TBP)_2$ they formulate with six coordinate uranium as:



Similar complexes are probably formed under our conditions.

[1] The U(VI) capacity of such gels has been found to be 74.6 ± 10% mg U/g dry SDVB.

[2] Since the TBP amount that can be embibed by SDVB has been found to decrease with the decrease of the TBP fraction in the swelling solution, it is to be expected that the TBP content of the HDEHP-TBP-gel used in these experiments would be lower than the assumed value and consequently the uranium amount that could be extracted by the TBP would be less than 74.6 mg/g dry SDVB.

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