

Extraction of uranium(IV) and uranium(VI) by primary and tertiary amines from sulphate solutions

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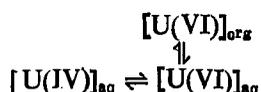
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Abstract. In developing a method for possible low level isotopic enrichment, which uses to advantage the equilibrium isotope effect observed during U(IV)-U(VI) electron exchange reaction in sulphate solutions, details of a solvent extraction process involving high concentration of a mixture of U(IV) and U(VI) and at low acid concentrations, are described. The extraction behaviour of uranium under these conditions is discussed. During the extraction with amines, U(IV) tended to get oxidised in sulphate solutions.

Keywords. Solvent extraction; uranium sulphate solutions; amines; three-stage extraction; extraction behaviour.

1. Introduction

In the past different solvent extraction procedures have been investigated for possible separation of isotopes of uranium, but met with little success (Hutchison 1952), both from the technological as well as basic science point of view. It has recently been observed (Peckett 1975), that a fast electron exchange takes place between U(IV) and U(VI) species in sulphate solutions ($H_2SO_4 = 0.08 M$), when the uranium concentrations are quite high ($U(VI) = 1.335 M$, $U(IV) = 0.1-0.4 M$). An isotope effect has also been reported to be taking place during the exchange reaction. An investigation was undertaken with a view to ascertain whether the isotope effect observed in electron exchange processes involving uranium in different valence states could be effectively utilised for the possible low level enrichment of uranium isotopes by a solvent extraction technique. To achieve this end, it is essential to develop a solvent extraction procedure, in which there is an equilibrium between U(IV) and U(VI) in the aqueous phase and between U(VI) in the aqueous phase and U(VI) in the organic phase.



This paper presents some of the results obtained while putting the above idea into practice.

2. Experimental

Primine JMT and alamine 336 were obtained from Rohm and Hass, USA, and General Mills, USA, respectively. They were used as received without further purification. Xylene used was of AnalaR grade.

Uranyl sulphate was prepared from pure U_3O_8 . U(IV) sulphate was prepared by electrolytic reduction of uranyl sulphate solutions in H_2SO_4 and obtaining the solid by adding excess alcohol. U(IV) sulphate had a composition $U(SO_4)_2 \cdot 8H_2O$.

In all experiments the organic phase was preequilibrated with appropriate concentration of sulphuric acid and centrifuged before contacting with aqueous phase containing uranium. The equilibration time throughout the investigation was 10 min and was carried out in a nitrogen atmosphere in cases where U(IV) was used. The organic to aqueous phase (volume) ratio was 1 : 1 in all cases, except in the 3-stage process to be described later.

U(VI) in the aqueous phase was estimated spectrophotometrically by measuring the optical density of its thiocyanate complex at 370 nm (Sandell 1959). U(IV) was estimated titrimetrically using standard $K_2Cr_2O_7$ solution (Rodden 1964). Mixture containing U(IV) and U(VI) were first estimated for U(IV) and later for total uranium by passing the mixture through a Jone's reductor and estimating the U(IV) once again titrimetrically. The extraction coefficient (D) was calculated from the aqueous phase concentrations before and after extraction.

U(VI) present in the organic phase, during the extraction of U(IV), was estimated by loading the amines with known quantities of U(VI) and drawing a calibration graph at 420 nm for primine JMT ($\epsilon_{420} = 25$) and at 460 nm for alamine 336 ($\epsilon_{460} = 23$). The optical densities of the organic phase equilibrated with U(IV) were measured at the respective absorption maxima and from the calibration graph, an estimate made of the amount of U(VI) present in the organic phase.

The 3-stage equilibration of U(IV)-U(VI) with 10% Alamine 336 in xylene is represented schematically in figure 3. The organic phase was loaded initially with U(VI) to an extent of 0.3 M. The aqueous phase of 0.08 M H_2SO_4 containing 0.1 M U(IV) and different amounts of U(VI) was contacted with U(VI)-loaded organic phase (aq : org = 1 : 5) in such a way that each phase was contacted with a fresh phase in any given operation. The U(IV) and U(VI) concentrations at the end of each equilibration (represented by \rightleftharpoons in figure 3) were estimated as described earlier.

3. Results and discussion

As outlined in § 1, the main emphasis in the present study has been to develop a solvent extraction procedure, that might prove useful in technology, and to study the behaviour of uranium species under the equilibrium conditions stated earlier.

Extraction behaviour of U(VI) by amines from sulphate solutions has been a subject of much discussion and data are available in literature (Catrall and Slater 1973). On the contrary the extraction of U(IV) from sulphate solution

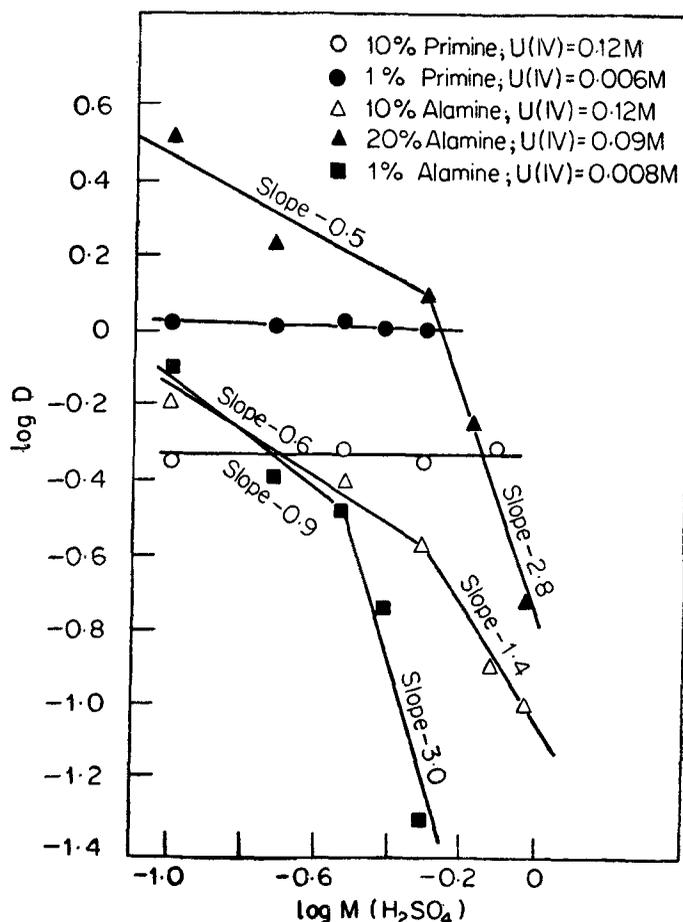


Figure 1. Effect of sulphuric acid concentration on the extraction of U(IV).

has not been that intensively studied. In figure 1, the extraction of U(IV) from different initial sulphuric acid concentrations in aqueous solution is shown. The extraction behaviour for alamine 336 can be clearly divided into two, having different slopes, while for primine JMT, the extraction of U(IV) is almost independent of the sulphuric acid concentration. It is possible to explain the reduction in extraction with increasing concentration of acid as arising out of the presence of bisulphate of the amines (Muller 1967). But the difference in the extraction behaviour among the two amines suggests that some other effect also plays a significant role during the extraction process.

Visible spectra of the U(IV)-extracted organic phase showed absorption at 655–660 nm and 550 nm characteristic of U(IV) species and a series of absorption between 420 and 480 nm characteristic of U(VI). For primine JMT maximum absorption for U(VI) occurred at 420 nm, while for alamine 336, it was at 460 nm.

Figure 2 shows the extent of oxidation of U(IV) during extraction, using primine JMT and alamine 336. Oxidation was more pronounced in the case of alamine 336 than with primine JMT. The tendency of U(IV) to oxidise during extraction

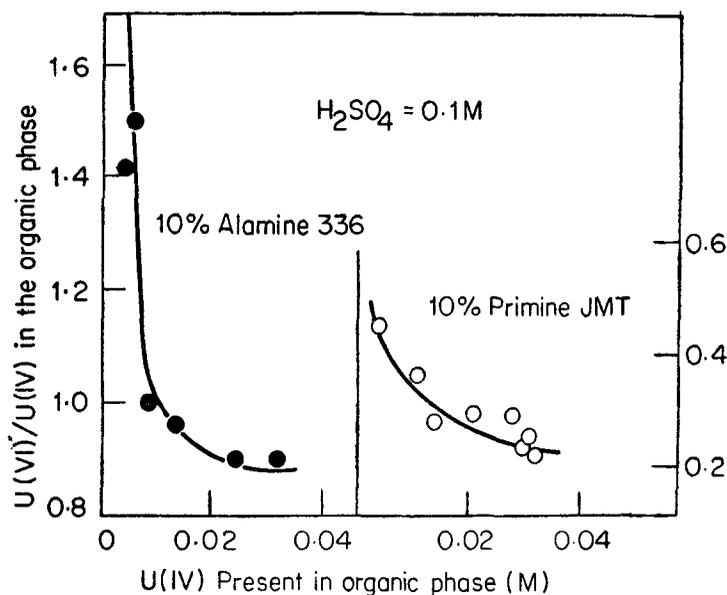


Figure 2. U(VI) present in the organic phase during the extraction of U(IV) by amines.

could be a reason for the difference in the extraction behaviour observed for the two amines (figure 1). It is also known that in sulphate solution the rate of U(IV)–U(VI) electron exchange is more and is reduced with increase in acid concentration (Ekstrom *et al* 1974).

The above observation needs an extensive investigation, and they have a bearing on the study in which a mixture of U(IV) and U(VI) species is involved. It should be mentioned that in many investigations reported in literature (Crouse *et al* 1956; Muller 1967; Schmid and Junger 1973; Wilson and Kedar 1961) on the extraction behaviour of U(IV), do not take this aspect of oxidation of U(IV) during extraction, both while reporting as well as interpreting the data, which need a careful reassessment.

In an attempt to develop a multi-stage solvent extraction process to achieve the equilibrium described in § 1, a 3-stage solvent extraction process was studied. The choice of the concentrations of uranium was based on the kinetic studies on the U(IV)–U(VI) electron exchange reaction (Peckett 1975). However, in the present study the concentration of U(VI) was fixed from the point of view of problems involved in handling the solution, such as viscosity of the extractant, crystallisation and encrustation of the concentrated aqueous solution, etc.

Figure 3 schematically represents the concentration changes occurring during each stage for a 3-stage solvent extraction process. There was an increase in the concentration of U(VI) in the aqueous phase at the end of the 3-stage process (represented by as ‘+’ in the last row of figure 3) and decrease in the concentration of U(VI) in the organic phase (denoted by ‘–’ in the last column of figure 3). Unlike the individual extraction of U(IV), in the 3-stage process,

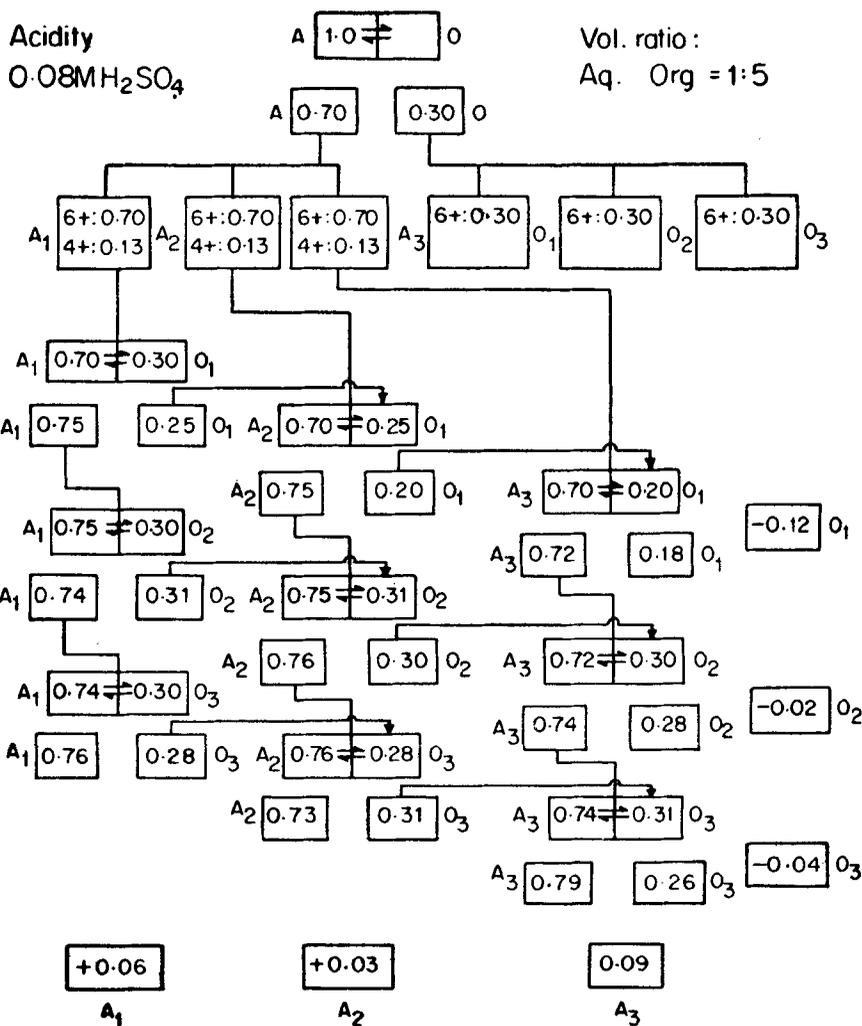


Figure 3. U(VI) concentration changes during a 3-stage process with 10% alamine 336 and U(IV)-U(VI) mixture.

U(IV) concentration did not change significantly throughout and hence its values are given only in the starting aqueous solution (figure 3).

In order to find out whether the 'leaching' of uranium from the organic phase is a concentration effect, the U(VI) concentration in the aqueous phase was varied keeping the U(IV) concentration constant. The organic phase was loaded with U(VI) to an extent of 0.3 M. The organic and aqueous (containing a mixture of U(IV) and U(VI)) phases were equilibrated only once. A plot showing the effect of U(VI) concentration on 'leaching' or 'extraction' is shown in figure 4. At lower concentrations, U(VI) had a tendency to get extracted into the organic phase, while at higher concentrations it tended to leach into the aqueous phase. In order to achieve an equilibrium which is sought to be maintained through as

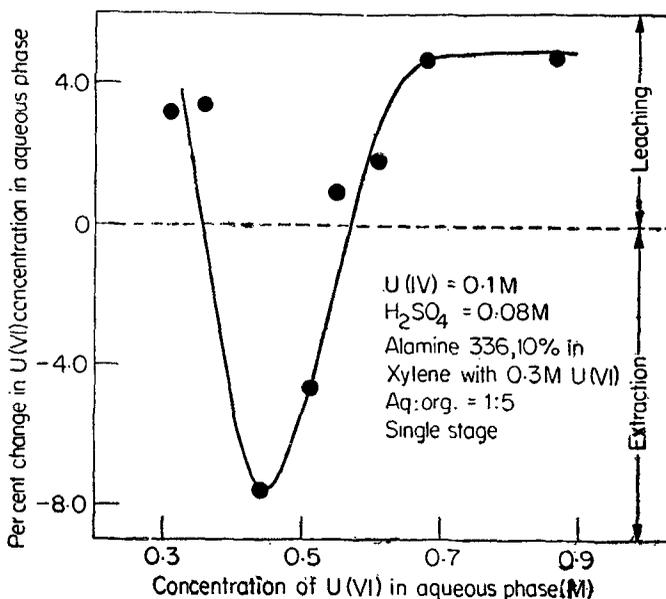


Figure 4. Effect of U(VI) concentration on extraction/leaching of U(VI) into/from U(VI) loaded alamine 336 in single stage.

many stages as possible, it would be ideal to work with a concentration of U(VI) where neither leaching nor extraction takes place as a result of equilibration. The plot in figure 4 indicates that these concentrations could be 0.35 M and 0.55 M of U(VI).

Based on the above observation a 3-stage extraction equilibration was carried out in the same manner as shown in figure 3. In all the experiments, U(IV) concentration was maintained at 0.1 M and H_2SO_4 concentration at 0.08 M. No significant change in U(IV) concentration was observed at any stage during the experiment. In figure 5, the concentration change in U(VI) at the end of each stage is plotted as a function of U(VI) concentration initially present in the aqueous phase. In the first two stages, the extraction and leaching of U(VI) followed the same pattern as shown in figure 4. But during the third stage, U(VI) tended to leach at all the initial concentrations. If the number of stages is increased, the U(VI) leaching from the organic phase is likely to increase and hence feed can be through the organic phase in a multi-stage process.

Results indicate that while developing a multistage extraction process for the possible low level enrichment of uranium isotopes, based on the optimum concentrations of uranium when the rate of U(IV)-U(VI) electron exchange reaction is high and when simultaneously an isotopic effect is also observed, leads to problems related mainly to the high concentration of solutions (both aqueous and organic) involved and also the large inputs of uranium required to achieve a meaningful separation. The extraction behaviour of uranium during a multi-stage process does not follow any predictable trend and the high uranium concentrations used still complicate the situation.

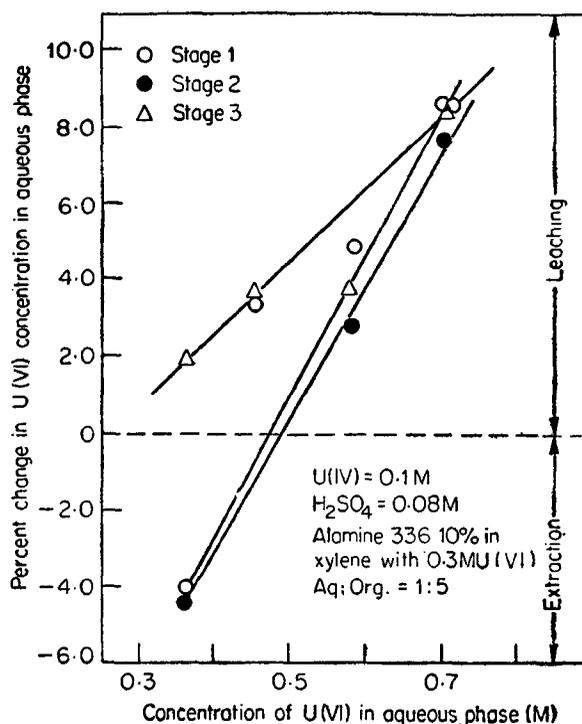


Figure 5. Effect of U(VI) concentration on extraction/leaching of U(VI) into/ from U(VI) loaded alamine 336 in a 3-stage process.

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