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EFFECT OF URANIUM ON THIRD PHASE FORMATION IN THE Pu(IV)-HNO_3-TBP-DODECANE SYSTEM

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ABSTRACT

Third phase formation is an important phenomenon which must be taken into account while designing flowsheets for fast reactor fuel reprocessing, since this phenomenon limits the plutonium loadings in the Tri-n-Butyl Phosphate(TBP) phase. In an earlier paper, the limiting organic concentration (LOC) of Pu(IV) above which third phase formation occurs was reported for the Pu(IV)-HNO_3-TBP system. In the present work, the effect of uranium on third phase formation in the Pu(IV)-HNO_3-30 % TBP-n-dodecane system was studied in detail at different acidities at 303 K. The LOC decreased with organic loading of uranium at all acidities studied.

INTRODUCTION

Third phase formation is an important phenomenon which limits the maximum organic phase loading of plutonium in extractions with Tri-n-Butyl Phosphate (TBP). Thus, third phase formation could limit the throughput of a reprocessing plant. The possibility of third phase formation assumes greater importance in the case of fast reactor fuel reprocessing, where higher concentration levels of plutonium are encountered.

The Fast Breeder Test Reactor (FBTR) at IGCAR, Kalpakkam uses a plutonium-rich carbide (Pu/(U+Pu) = 0.7) as the driver fuel. To design a Purex-type flowsheet for reprocessing FBTR fuel, it is necessary to have detailed information on third phase formation in the U(VI)-Pu(IV)-HNO_3-TBP system. A programme on the determination of limiting organic concentration (LOC) of plutonium as a function of various parameters has been initiated in this laboratory. The results obtained on third phase formation in the Pu(IV)-HNO_3- TBP system were reported earlier (1).

The presence of U(VI) in the organic phase would modify the properties of the TBP phase and would therefore result in changes in third phase formation characteristics. It is necessary to have a knowledge of the LOC of plutonium as a function of the organic loading of U(VI) to enable suitable modification of the flowsheet. The only data available in the literature are those reported by Kolarik and co-workers (2,3). However, their conclusions were based on a limited number of experimental points. It was therefore felt desirable to study in detail third phase formation in the U(VI)-Pu(IV)-HNO_3-TBP system.

In this paper, the LOC values for Pu(IV) obtained as a function of equilibrium aqueous nitric acid concentration and U(VI) loading in the organic phase are reported.

EXPERIMENTAL

TBP was obtained from M/S Fluka and purified by the method suggested by Alcock et al.(4). Commercial grade n-dodecane was used as received for preparing 30 % TBP solutions. Uranyl nitrate hexahydrate ($UO_2(NO_3)_2.6H_2O$) supplied by M/S British Drug House (UK) was used to prepare 0.5 M nitric acid stock solutions containing 50 mg/ml to 100 mg/ml of U(VI). Plutonium nitrate was purified from Am-241 by an anion exchange method. A concentrated stock solution of plutonium (100 mg/ml) was used in all the experiments. The oxidation state of plutonium in the stock solution was adjusted to Pu(IV) with NO_2 and was confirmed by extraction tests with 0.5 M 2-Thenoyltrifluoroacteone (HTTA) in benzene.

All other chemicals used were of Guaranteed Reagent grade.

The experimental apparatus consisted of a flat-bottomed tube kept in a thermostatted vessel. Water from a constant-temperature bath was circulated through the vessel. Mixing of the aqueous and organic phases was accomplished by a teflon-coated magnetic stirring bar. The temperature of the bath was maintained at 303 ± 0.1 K in all the experiments.

Determination of LOC

The third phase was first formed by equilibrating the TBP solution with concentrated Pu stock solution. The aqueous phase was removed after centrifugation. The third phase was then dissolved by the addition of uranyl nitrate solution as well as nitric acid solution. By controlling the addition of these solutions, the exact point at which the third phase dissolved completely was reached. By choosing properly the concentration of the uranyl nitrate and the nitric acid solutions and by varying the volumes of the solutions added for the dissolution, the equilibrium aqueous acidity as well as the uranium loading in the organic phase could both be controlled. The phases were mixed thoroughly in between solution additions to ensure that equilibrium was achieved and that the temperature of the phases reached that of the thermostatted vessel. The dissolution of the third phase could be easily followed visually since its dark brown colour is distinctly different from that of the light organic as well as the aqueous phase.

Plutonium and uranium concentrations in the organic and aqueous phases were determined (3) as follows: A suitable aliquot of the aqueous phase was added to a beaker containing 15 ml of 0.05 M nitric acid and titrated with a solution of diethylene triamine pentaacetic acid (DTPA) using xylenol orange as the indicator. Care was taken not to add an excess of DTPA. Subsequently, the pH of the solution was adjusted to 3.6 using sodium hydroxide solution and 5 ml of sodium acetate- acetic acid buffer (pH 3.6) was added to the beaker. Estimation of uranium was carried out by titrating against 2:6 pyridine dicarboxylic acid using Arsenazo I as the indicator.

Organic aliquots were pipetted into a beaker containing 15 ml of 0.05 M nitric acid. The pipette was washed with methanol, and the washings were also transferred into the beaker. Determination of plutonium and uranium was carried out as described above.

The free acidity of the aqueous phase was determined by titrating against standard sodium carbonate solution after complexing plutonium and uranium with sodium sulphate (5).

RESULTS AND DISCUSSION

The data on LOC as a function of organic phase uranium loading at "nominal" equilibrium aqueous acidity of 2.4 M, 3.3 M, 4.0 M, 4.8 M and 5.4 M are given in figures 1 to 5. Since it is practically impossible to reach pre-determined values of the organic uranium loading as well as the equilibrium acidity, the actual equilibrium concentrations of uranium and nitric acid were determined in each experiment, and these values were found to be within about 10-15 % of the "nominal" values quoted in the figures. The actual ranges of values are indicated in the figure legends. To take into account the variation in the LOC value at zero uranium loading due to this variation in acidity, the "zero" LOC values are represented as a band in Fig.1 to 5. For figures 4 and 5, the "zero" LOC values from Kolarik's work (2) have been used. The possible course of variation of LOC with uranium loading in TBP is indicated by a curve starting from the middle of the band of "zero" LOC values.

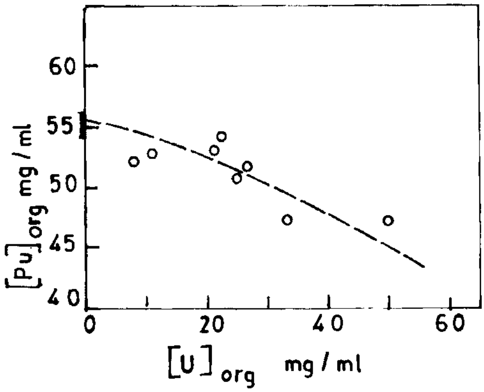

Fig. 1. Variation of LOC of Pu with equilibrium uranium loading in TBP, at a nominal equilibrium aqueous acidity of 2.4 M. (2.19 M to 2.59 M).

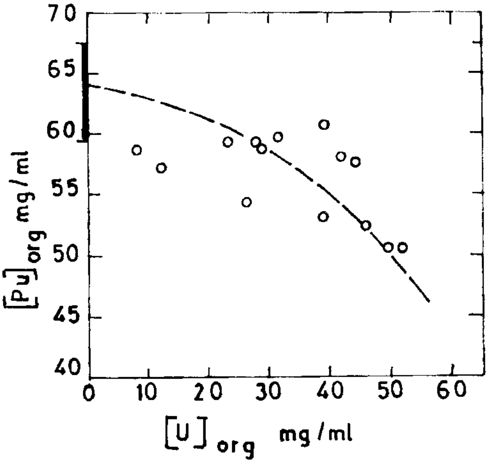

Fig. 2. Variation of LOC of Pu with equilibrium uranium loading in TBP, at a nominal equilibrium aqueous acidity of 3.3 M. (2.93 to 3.58 M).

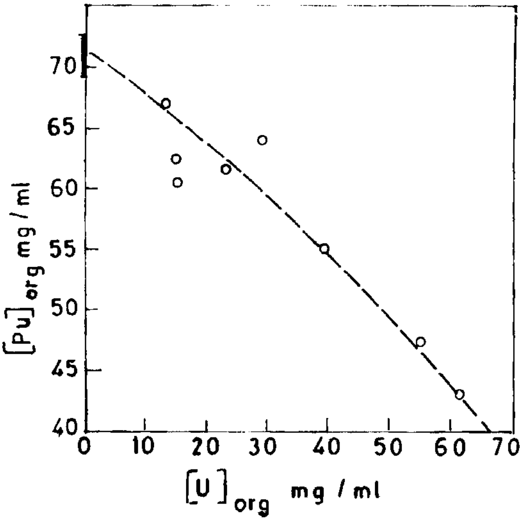

Fig. 3. Variation of LOC of Pu with equilibrium uranium loading in TBP, at a nominal equilibrium aqueous acidity of 4.0 M. (3.82 M to 4.27 M).

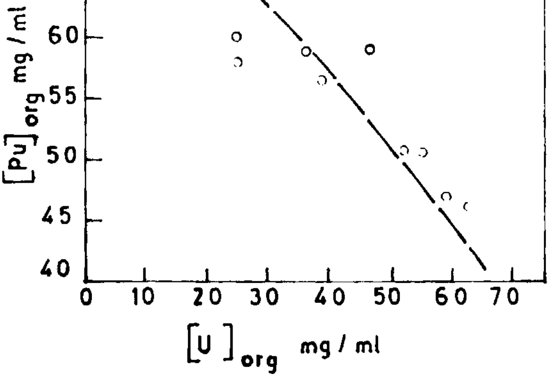

Fig. 4. Variation of LOC of Pu with equilibrium uranium loading in TBP, at a nominal equilibrium aqueous acidity of 4.8 M. (4.47 M to 5.04 M).

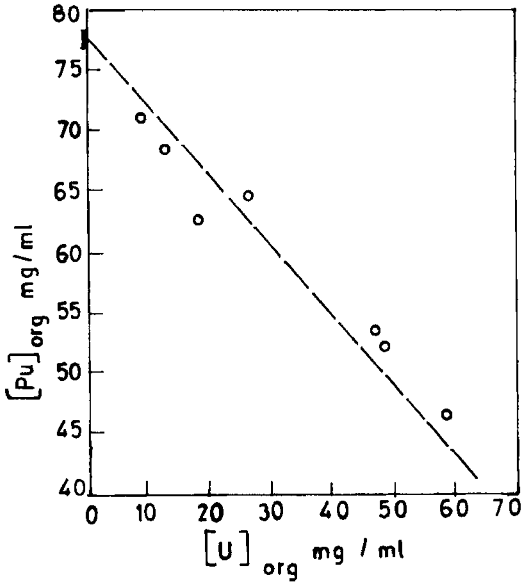

Fig. 5. Variation of LOC of Pu with equilibrium uranium loading in TBP, at a nominal equilibrium aqueous acidity of 5.4 M. (5.1 M to 5.73 M).

The LOC values are seen to decrease with increasing uranium loading in the TBP phase, at all the acidities studied. The decrease in the LOC values is more pronounced at higher acidities.

Figure 6 includes data on the variation of LOC with equilibrium aqueous acidity at organic phase uranium loading of 19 ± 4.5 mg/ml and 50 ± 3.5 mg/ml. Also included for comparison are our data for zero uranium loading at 303 K, as well as Kolarik's data for zero uranium loading (3) at 304 K. There is some disagreement between the "zero" values in the range of 1 to 2 M acidity. However, the agreement is satisfactory at higher acidities. (This justifies our use of Kolarik's "zero" LOC values in Fig. 4 and Fig.5). The figure clearly shows a decrease in LOC due to the loading of U(VI) in the TBP phase, the difference increasing at higher acidities.

Kolarik's data for an equilibrium aqueous acidity of 3.0 M (2) show an increase of LOC values at uranium loadings up to about 30 mg/ml and a subsequent decrease in the LOC value at

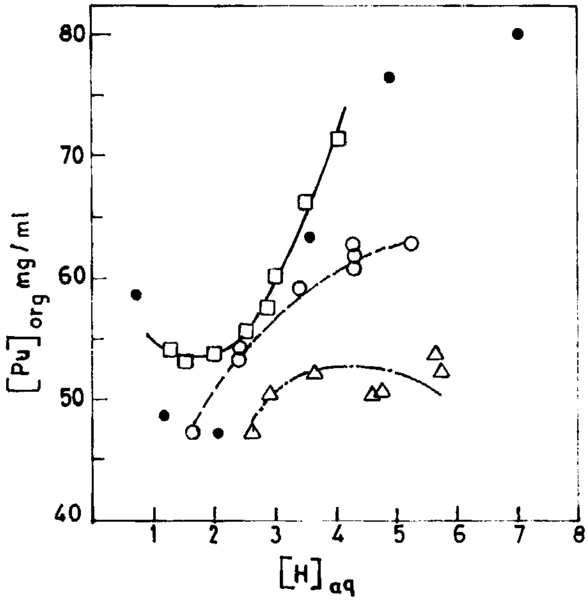

Fig. 6. Variation of LOC of Pu with equilibrium aqueous acidity.

□ : Our values for zero uranium at 303 K;

● : Kolarik's values for zero uranium at 304 K;

○: Our values at a nominal organic uranium loading of 19 mg/ml.

△: Our values at a nominal organic uranium loading of 50 mg/ml.

higher loadings. Subsequent data reported by Nakashima and Kolarik (3) suggest that when the uranium loading of the TBP phase is about 60 mg/ml, the LOC values are higher than those in the absence of uranium, for aqueous acidity ranging from 2 to 4 M. (At acidities higher than 4 M, their data indicate a decrease in LOC with uranium loading). However, the inference by Nakashima and Kolarik is based on a limited number of experimental points. Further, their data were obtained at 298 K, whereas the temperature in our experiments was 303 K. Our data cover a wide range of acidities and uranium loadings in the organic phase, and a clear trend of decrease in LOC with uranium loading can be seen.

Our conclusion is also supported by the observation that any factor that reduces the free TBP concentration should reduce the

LOC. For example, the effect of U(VI) on third phase formation in Th(IV) and U(IV) systems show a trend similar to ours for the Pu(IV) system (3). Extraction of nitric acid into TBP is also known to decrease the LOC values, except in the case of Pu(IV)-HNO_3-TBP system, where, perhaps, there is some specific interaction between the Pu complex and HNO_3 complex species.

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