A Study of the Third Phase Formation in the Extraction of U(IV) in TBP-HCl System Using Toluene and Kerosene as Diluents

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Abstract

The extraction of U (IV) in TBP – HCl system, using toluene and kerosene as diluents, was studied. When toluene was used, a single organic phase appeared at all hydrochloric acid concentrations. The extracted species at high [HCl] which is 5-8 M could be a mixture of UCl4-TBP and UCl4.3TBP. When kerosene was used at high [HCl] which was 5-8 M , two immiscible organic phases appeared. The experimental results in light organic phase indicated UCl4-TBP as extracted species while in heavy organic phase, UCl4-TBP was identified, and the UCl4-3TBP was insoluble in kerosene which lead to the formation of third phase.

Key words: Tetravalent Uranium , TBP ,Kerosene, Toluene

Introduction

In liquid - liquid extraction systems, the formation of third phase refers to the phenomenon whereby the original organic phase splits into two immiscible organic phases which mutually coexist with an immiscible aqueous phase. Third phase formation is a general phenomenon encountered in many different liquid-liquid extraction systems.

Early in 1959, Irving H. et.al. [1] studied the extraction of hydrochloric acid with TBP-kerosene system. They found that above 5 M aqueous hydrochloric acid concentration, three phases were separated, the upper, most of kerosene containing very little water or acid, and a middle layer of TBP saturated with water and hydrochloric acid but containing little kerosene

Third phase formation in the extraction of HCl tri-n-butyl phosphate (TBP) in n-octane had been investigated in 2006 by Chiarizea R. et.al. [2] who found that the extraction of acid is accompanied by the simultaneous extraction of large amounts of water and brings about organic phase splitting when the equilibrium HCl concentration in the aqueous phase is higher than 7.6 M. Third phases were formed and investigated in the extraction of Th(IV) by TBP/n-dodecane [3] , Pu (IV) nitrate by 30% TBP [4] and U(IV) nitrate –TBP [5]. Speciation studies in third phase formation of U(IV) , Pu(IV), Th (IV) third phases in TBP systems, based on the spectroscopy has detected the presence of an extended solvate[6] . In the extraction of uranium nitrate, the presence of disolvate and trisolvate of $UO_2(NO_3)_2$ by TBP were detected [7], while by infrared studies of $UO_2(NO_3)_2$- 20% TBP in dodecane system , disolvate $UO_2(NO_3)_2$ by TBP was reported [8]. In the extraction of uranium tetrachloride by tri butyl phosphate in kerosene, the formation of UCl4.3TBP [9] and UCl4.2TBP [10] were observed.

The aim of this work is to study the mechanism of equilibrium reaction of uranium tetrachloride in TBP-HCl system using toluene and kerosene and extend this work to study the third phase formation.

Experimental

Reagents

Preparation of Tri-butyl phosphate in odorless kerosene and toluene:-

Tri-butyl phosphate (Fluka 99-98%) was diluted to 50% with odorless kerosene and toluene (BDH 99%) and purified by washing with an equal volume of 0.1 M sodium carbonate followed twice by an equal volume of 0.1 M hydrochloric acid .

Finally it was washed with distilled water until the aqueous phase was neutral.

Different concentrations of TBP (2.5-50%) were prepared by dilution of 50% TBP with calculated amount of odorless kerosene and toluene.

The organic phases were filtered using filter paper to remove settled water.

Preparation of Uranium (IV) solution

Ammonium-diurinate $(NH_4)_2U_2O_7$ (supplied by the Iraqi Nuclear Centre) was heated to 350°C to obtain UO_3. [11]

$$(NH_4)_2U_2O_7 \quad \xrightarrow{\quad \Delta \quad} \quad 2UO_3 + \ H_2O + 2NH_3$$
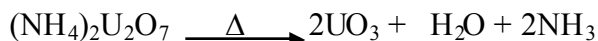
The UO_2Cl_2 stock solution was prepared by dissolving UO_3 in hydrochloric acid solution. Uranium tetra chloride solution was prepared by reduction of UO_2Cl_2 using mercury cathode electrolysis [12]. One molar UCl_4 was prepared in different hydrochloric acid concentrations (0.1-8.0 M HCl).

Measurements

Hydrochloric acid concentrations were measured by titration with NaOH in the presence of potassium fluoride (KF) [13]. Uranium (IV) concentrations were measured in both aqueous and organic phases using potentiometric titration method [14]. Low uranium (IV) concentration was measured using a spectrophotometric technique at 650 nm. Tributyphosphate concentrations in light and heavy organic phases were measured [15].

The distribution experiments were carried out in 50 ml test tubes sealed with polyethylene caps.

Fifteen millilitres ml of aqueous and organic phases were pipetted into the test tubes.The phases were equilibrated in mechanical shakers for 20-30 min at room temperature. The experiments were carried out in ordinary light and no precautions were taken to avoid influence of sunlight.

Result and Discussion

Tri-butyl phosphate- toluene system

The effect of contact time between organic and aqueous phases was studied in the extraction system of uranium (IV) 30% tri-butyl phosphate (TBP) in toluene and 3M hydrochloric acid (HCl) , initial uranium (IV) concentration was 1.14M .

The results are shown in Table 1. . These results reflected no significant effect of contact time on the extraction of U(IV)-TBP system , and the TBP concentration remain constant during the experimental time which indicates that the TBP exhibits no degradation.
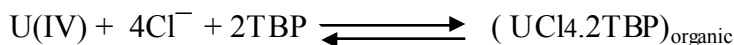
The distribution ratio of uranium (IV) between 30%TBP and HCl as a function of aqueous hydrochloric acid is revealed in Figure 1., for the initial aqueous uranium (IV) of 1M.

The distribution ratio increased gradually with the increase of acidity up to 7M HCl then it increased dramatically at 8M HCl . From this figure it was found that the best hydrochloric acid concentration for the extraction of uranium (IV) was between (3-4 M HCl) and also the best HCl concentration for stripping of uranium (IV) was < 0.1MHCl in application of industrial systems (like the pulsed column and the mixer settler).
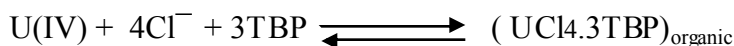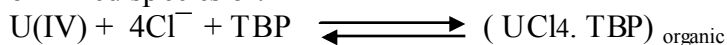
Figure2. Shows the logarithmic distribution ratios of uranium (IV) log Du at 1M initial Uranium(IV) concentration as a function of log. nominal TBP concentration for series of aqueous hydrochloric acid concentrations.

Straight lines with slops close the 1.75 were obtained by least square fit. From this slope value one can conclude that one or more species could be included in the extraction of Uranium (IV) in this system.

Accordingly one can estimate that the reaction mechanism could be as follows:

$$U(IV) + 4Cl^- + 2TBP \rightleftharpoons (UCl4.2TBP)_{organic}$$

or mixed species of:

$$U(IV) + 4Cl^- + TBP \rightleftharpoons (UCl4. TBP)_{organic}$$

$$U(IV) + 4Cl^- + 3TBP \rightleftharpoons (UCl4.3TBP)_{organic}$$

Tri-butyl phosphate- Kerosene system

On the extraction of Uranium (IV) by 30% TBP-Kerosene system, same behavior was observed as presented in Figure 1, but with the increase of hydrochloric acid concentration up to 5 M , second organic phase clearly appeared.

Table 2. shows the results of extraction system with different parameters [TBP], [HCl], and Uranium(IV) concentrations , It was found that these parameters played an important role in the appearance of this second organic phase . It also was found that at 2.5-5% and 5% TBP concentrations only single organic phase appeared, while with increased TBP concentration , a second organic phase clearly appeared and the volume ratio of the second organic phase to the volume of the total organic phase increased with the increase of TBP , HCl and Uranium (IV) concentrations .

Figure 3 shows the logarithmic distribution ratio (log Du) of Uranium (IV) in the heavy organic phase to the Uranium (IV) in the aqueous phase as a function of log measured TBP concentration in the heavy organic phase. A straight line with a slope close to 3 was obtained, which indicates that the mechanism of the reaction could be as follows:

$$U(IV) + 4Cl^- + 3TBP \rightleftharpoons (UCl4.3TBP)_{organic}$$
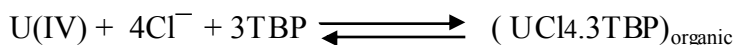
Probably this organic species is slightly dissolved in kerosene which explains the appearance of this second organic phase.

Figure 4 shows the logarithmic distribution ratio of Uranium (IV) concentration in the light organic phase to the Uranium (IV) concentration in the heavy organic phase as a function of log TBP concentration measured in light organic phase .A straight line with a slope close to one was obtained which indicated that the mechanism of the reaction could be as follows:
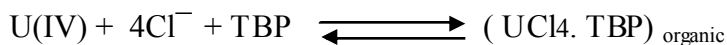
$$U(IV) + 4Cl^- + TBP \rightleftharpoons (UCl4. TBP)_{organic}$$

Figure 5. shows the relation between log organic U(IV) concentration and log aqueous U(IV)concentration , from this plot we can calculate the number of theoretical stages needed for the extraction .

Conclusions

In the extraction of U(IV) with TBP toluene , only single organic phase appeared, where mixed organic species involved in the extraction of U (IV) with TBP-toluene-HCl system.

In the extraction of U(IV) with TBP-kerosene-HCl system, two organic phases appeared at high U(IV) and HCl concentration .

In TBP- HCl –kerosene system with low TBP concentration 2.5% and 5%, single organic phase appeared. The volume of heavy organic phase layer increased with the increase of HCl, U (IV), TBP concentrations.

The result of extraction of U(IV) in TBP-kerosene system indicates two species UCl4.3TBP and UCl4.TBP involved in the extraction system.

The species UCl4.3TBP was insoluble in kerosene, hence a second immiscible organic phase was formed.

From our results, we recommend that the best condition for the extraction of U(IV) in TBP-kerosene-HCl system in industrial applied systems should be as follows, the initial concentration of , HCl $\leq$ 3.0M , [U(IV)] $\leq$ 1M , and 30% TBP in order to avoid third phase formation which disturbs the extraction system .

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Table (1): The effect of contact time on the extraction of U(IV) using 30%TBP - toluene， [HCl]$_{initial}$=3M, [U(IV)]$_{initial}$=1.14M at room temperature.

Contact time	Du	Measured [TBP]%
15 min	0.303	30±1.2
6 hr	0.297	30±1.2
12 hr	0.3	30±1.2
18 hr	0.295	30±1.2
24 hr	0.304	30±1.2

Table(2): Experimental data of different TBP%, different [HCl]M, Volume ratio of 2nd organic phase to the total organic phase and [U(IV)] in both light and heavy organic phases.

| [TBP] %	[HCl] M	Vol.of 2nd org. phase/ Vol. of total org. phase	[U] in light org. phase	[U] in 2nd org. phase
2.5	5	Single org. phase appears	8.902	Single org. phase appears
5	5	=	16.257	=
10	5	=	30.153	=
20	5	0.1	39.98	44.59
30	5	0.24	53.396	200.468
2.5	6.5	Single org. phase appears	8.186	------
5	6.5	=	16.6314	------
10	6.5	0.04	16.527	18.36
20	6.5	0.2	18.788	273.68
30	6.5	0.32	23.755	276.83
40	6.5	0.54	21.962	249.86
2.5	7.4	Single org. phase appears	10.475	-------
5	7.4	=	14.591	------
10	7.4	0.08	15.546	15.74
20	7.4	0.24	16.144	279.38
30	7.4	0.38	17.911	278.70
40	7.4	0.5	21.187	266.69
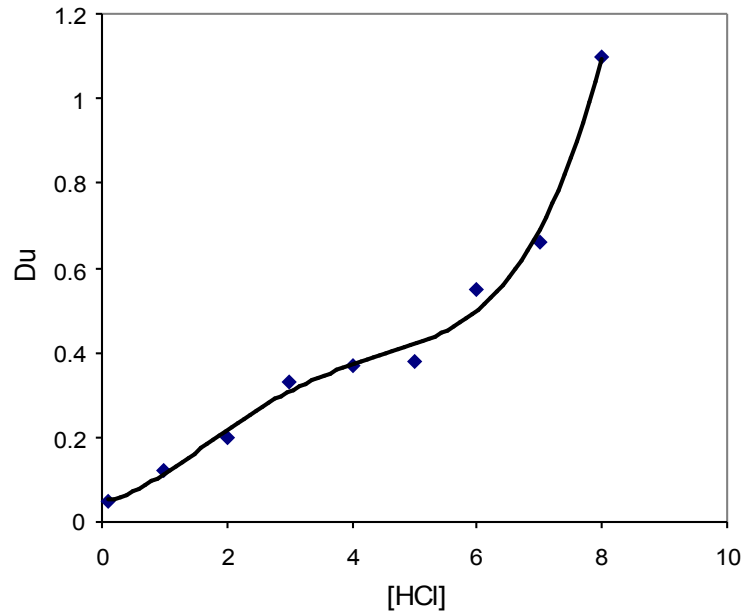
Fig. (1): Distribution ratio of U(IV) in 30%TBP-toluene - HCl system as a function of aqueous [HCl] for 1M aqueous [U(IV)]$_{initial}$
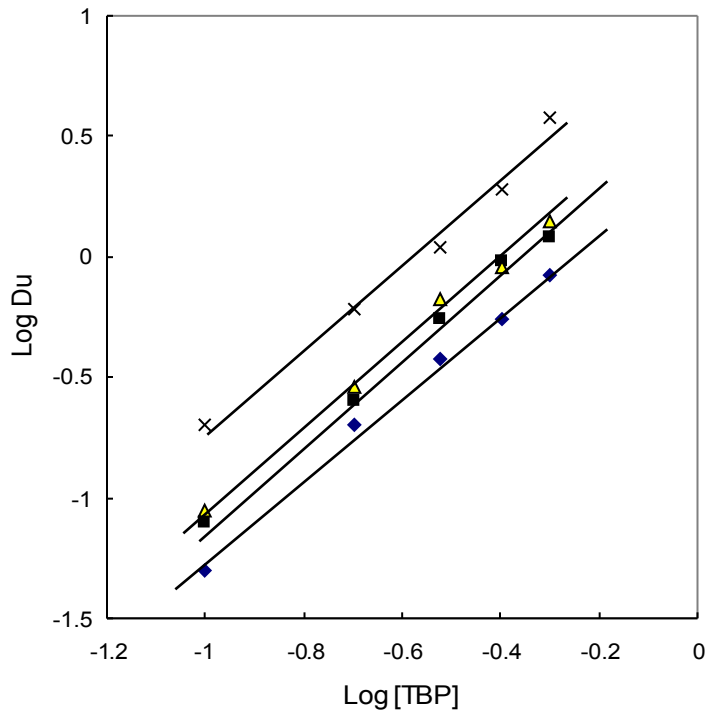

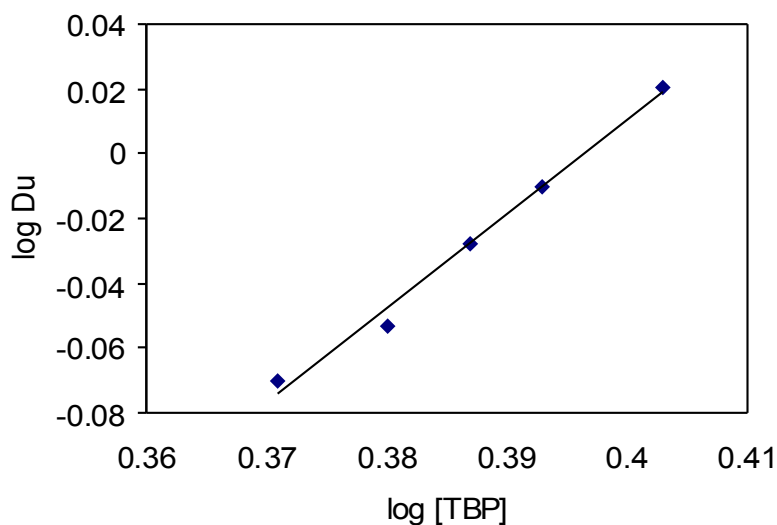**Fig.(2) : Log distribution ratio of U(IV) as afunction of Log nominal TBP concentrations in ♦5M, ■6M, Δ7M and in ×8M HCl .**

Fig.(3):The log Du of [U(IV)] in heavy organic phase to [U(IV)] in aqueous phase as a function of log [TBP] in heavy organic phase, A straight line with a slope close to 3 was obtained
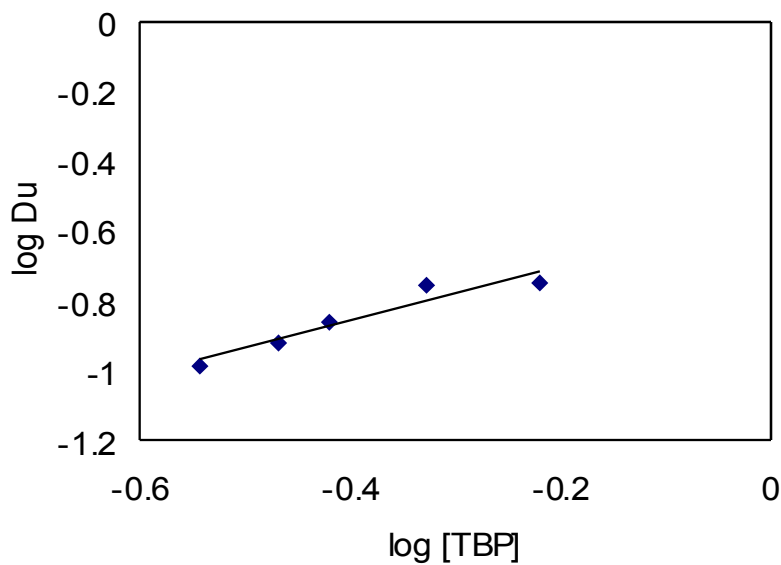

Fig.(4) :LogDu of [U(IV)] in light organic phase to [U(IV)] in heavy organic phase as a function of log measured [TBP]. A straight line with slope close to one was obtained
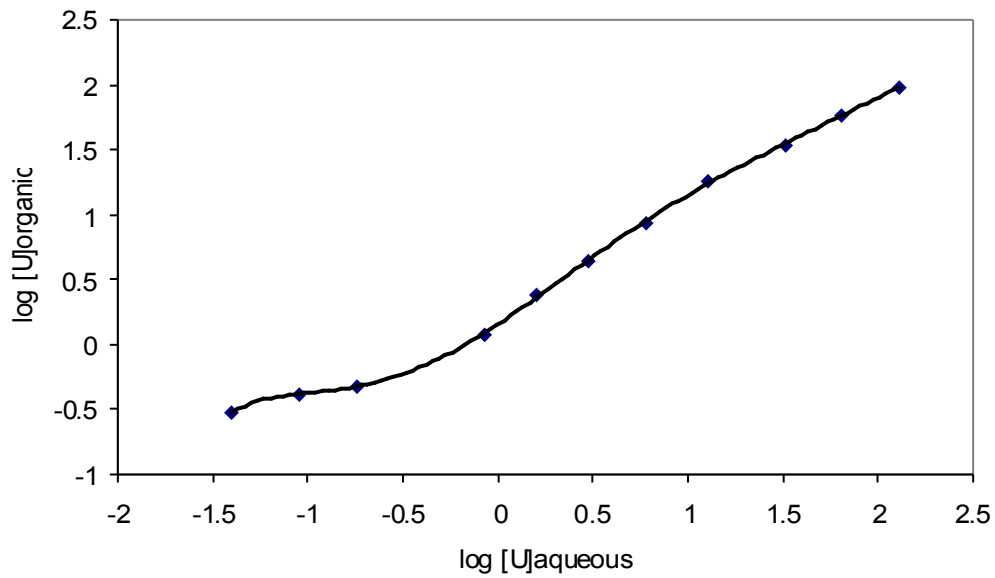
Fig. (5): log[U]organic as a function of log[U]aqueous using 30% TBP in kerosene and [HCl] aqueous = 3M with different initial U(IV)concentrations.

دراسة تكون الطبقة العضوية الثالثة في الاستخلاص المذيبي لليورانيوم الرباعي في منظومة ثالث بيوتيل الفوسفات – حامض الهيدروكلوريك باستعمال التولوين والكيروسين محففات عضوية

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الخلاصة

درس الاستخلاص المذيبي لليورانيوم الرباعي في منظومة ثالث بيوتيل الفوسفات – حامض الهيدروكلوريك باستعمال التولوين والكيروسين مخففات عضوية.

عند استعمال التولوين مخفف عضوي ظهرت طبقة عضوية واحدة واشارت نتائج التجارب الى وجود خليط من الاصناف الكيميائية الأتية UCl_4-TBP ،   وUCl_4-3TBP في تراكيز حامض الهيدروكلوريك (M 8-5). بينما عند استعمال الكيروسين مخفف عضوي ظهرت طبقتان عضويتان غير ممتزجتين فضلا عن الطبقة المائية مما يشير الى تكوين طبقة ثالثة .

اشارت النتائج في الطبقة العضوية الخفيفة الى تكون الصنف الكيميائي (UCl_4-TBP) ، بينما في الطبقة العضوية الثقيلة تكون(UCl_4-3TBP) ،وهذا الصنف تكون ذوبانيته في الكيروسين محدودة مما يؤدي الى ظهور الطبقة الثالثة.

الكلمات المفتاحية : اليورانيوم الرباعي ، ثالث بيوتيل الفوسفات، كيروسين ، تولوين