

Mass Transfer of U(IV) in HCl-TBP System Employing Free Falling Single Drop Technique in Different Diluents

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Abstract

In this work free falling drop technique has been utilized to study the mass transfer kinetics of U(IV) in 30% TBP-HCl system using different diluents, namely kerosene, toluene and (LAB+BTX) which is a mixture of equal volumes of linear alkyl benzene (LAB), and isotropic mixture of benzene, toluene and xylene (BTX). The concentrations of hydrochloric acid and U(IV) in the aqueous phase were 3.4-7.2 M and 1M, respectively. It was found that the kinetic rates increased with increasing the aqueous hydrochloric acid concentration and drop diameters.

Furthermore, the results revealed an increase in the activation energy (E_a) according to the diluent's nature and followed the sequence, (LAB + BTX) < toluene < kerosene. Also the physical properties of the diluents influenced the rate constant of U(IV) extraction, which increased in the order :

kerosene < toluene < (LAB+BTX) .

Keywords: Mass transfer, Tetra-valent uranium, Tri-n-butyl phosphate, Hydrochloric acid.

Introduction

Mass transfer rate studies have almost exclusively been made in systems involving uranyl nitrate and tributyl phosphate (TBP). Centrifugal extractors [1], extraction cells with a quiescent interface and stirred [2] or unstirred phase [3] liquid single drop [2,4] have been applied.

The rate of the uranyl nitrate extraction by tri-n-octylphosphine oxide (TOPO) has been studied by the single drop method [5]. All the transfer rates measured were found to be first order in the metal concentrations [5,6].

The rate of mass transfer of uranium (IV) chloride between aqueous hydrochloric acid solutions and TBP or TOPO in cyclohexane has been determined using the single drop technique. First order with respect to the concentration of U(IV) and TBP or TOPO were obtained [7].

Single drop technique also has been applied to uranium isotope transfer between free ions dissolved in an aqueous phase and the corresponding complexes of an organic phase [8]. The kinetics of solvent extraction of U(IV), Th(IV) and U(VI) from nitric acid solution with TBP in kerosene and cyclohexane have been studied using the single drop technique [9]. In centrifugal extraction it has been established that the rate of uranium, plutonium in nitric acid extraction

from TBP, is diffusion controlled.[5]. A model for the drop mass transfer coefficient has been developed.[10]

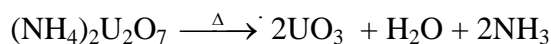
Recently single drop technique has been applied on the kinetics of solvent extraction of zirconium (IV)[11] and copper(II).[12]

The aim of the present work is to extend our knowledge in UCl₄ mass transfer in TBP and hydrochloric acid extraction system using the following parameters : variable acid concentration, different diluents, variable temperatures and different drop diameters.

Experimental

Reagents:

Ammonium diuranate (NH₄)₂U₂O₇ (supplied by the Iraqi Nuclear Centre) was heated to 350 °C to obtain UO₃. [13]



The UO₂Cl₂ stock solution was prepared by dissolving UO₃ in hydrochloric acid solution.

Uranium tetra chloride solution was prepared by reduction of UO₂Cl₂ using mercury cathode electrolysis [14]. One molar UCl₄ was prepared in HCl solution of different concentrations (3.5, 4.0, 5.0, 6.0, 7.0 M HCl).

The organic solutions of TBP (Fluka, 99-98%) were prepared by dilution with

practical grade odorless kerosene, toluene and a mixture of equal volumes of linear alkyl benzene (LAB) and isotropic mixture of benzene, xylene and toluene (BTX), (Arab Company of Chemical Detergents., Baiji, Iraq).

The organic solutions were purified following Alcock et al. procedure [6]. The concentration of UCl_4 was measured using potentiometric titration method [15]. Hydrochloric acid concentration was measured by titration with NaOH in the presence of potassium fluoride (KF) [16].

Measurement of the Transfer Rate :

Falling single drop measurements were carried out using organic phase as the continuous phase and the aqueous phase as the dispersed phase. Calibrated falling drops were obtained using a digital automatic burette (type Dosimat, Metrohm). To achieve different travel drop time, different column lengths (19, 28, 37 and 58 cm) were used.

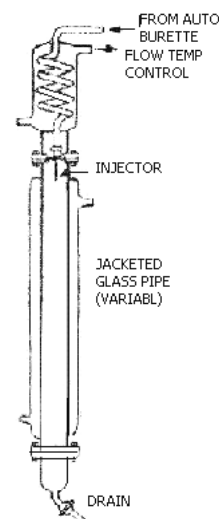


Fig.(1) Falling drop arrangement.

Fig.(1) shows the employed technique. In order to get different drop diameters, different injector diameters had been employed. Circulated water bath was used to ensure a constant temperature.

The densities of mixtures of 30% TBP in different used diluents were measured using the gravimetric method, and their viscosities were measured by a viscometer (type : falling sphere; 2440, jpg.).

Results and Discussion

The following equation was used to calculate the mass transfer of U(IV). [7]

$$dC_{aq}/dt = - (A_s/V_a) K C_{aq}$$

Where:
 dC_{aq} = no. of moles of the transferred solution into organic phase

V_a = drop volume.

A_s = interfacial area

K = mass transfer rate

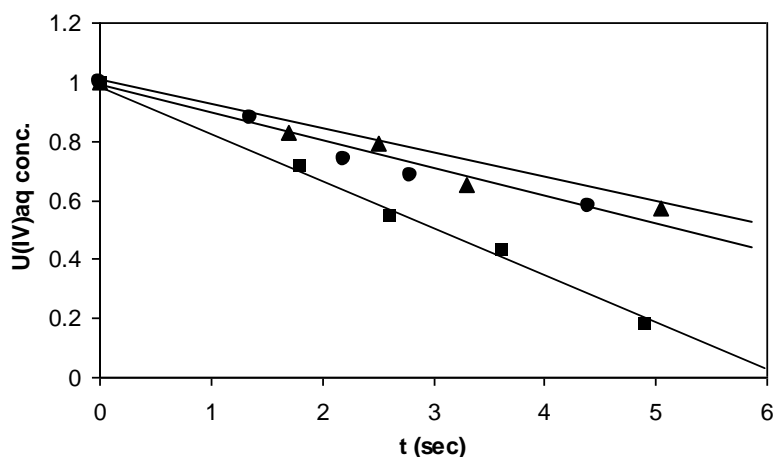


Fig.(2) Aqueous U(IV) concentration against drop travel times (t) using 30% concentrations with different diluents: ▲ kerosene, ● toluene and ■ LAB+BTX, $[U(IV)]_{initial} = 1 M$, $[HCl] = 4M$ at $20^{\circ}C$.

Fig.(2) Presents uranium concentration post mass transfer as a function of drop travel time. Organic phases which devoted were, 30%TBP/ odorless kerosene, toluene and equal volumes of BTX and LAB. Uranium concentration in the aqueous phase slightly decreased with travel time when odorless kerosene was used as a diluent compared to toluene. While aqueous uranium concentration

decreased dramatically with travel time when (LAB + BTX) was employed as a diluent with TBP in comparison to both odorless kerosene and toluene. This indicates that the nature of diluents plays a significant role in the mass transfer rate of U(IV) which increases in the following sequence:

odorless kerosene, toluene and (LAB + BTX)

Table (1)

The physical properties of 30% TBP in diluents and the extraction rates of U(IV) in 4M HCl at 20°C.(drop diameter 0.25 cm).

Diluents	Viscosity (c.p)	Density (g/ml)	Extraction rate (mole/cm.s)
Kerosene	1.5165	0.80027	0.00365
Toluene	0.8243	0.8871	0.00415
LAB+BTX	2.1658	0.89906	0.00692

From Table (1) one concludes that the physical properties, density, viscosity and nature of diluents have important impacts on the extraction rate of U(IV), which is explicitly shown in the case of (LAB+BTX).

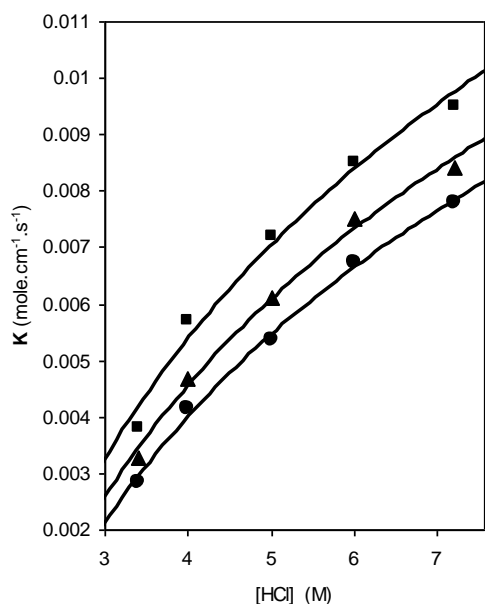


Fig. (3) Plots of the mass transfer rate constants of U(IV) as a function of [U(IV)]_{aq} with different drop diameters : ● 0.25, ▲ 0.3 and ■ 0.35 cm at 20° C.

Fig.(3) exhibits the mass transfer rate constant of U(IV) as a function of aqueous hydrochloric acid concentration (3.4-7.2 M) using different calibrated drop diameters (0.25,

0.3, and 0.35 cm). In this figure we observe that the mass transfer rate constant of U(IV) increases significantly with the increase of aqueous hydrochloric acid concentration. On the other hand, the mass transfer rate constant increases as the drop diameter has increased.

The increase of mass transfer rate constant with increasing of the drop diameter could be due to the change in drop motion. It was postulated that the drop motion changes smoothly from being stagnant to vigorously circulating as drop diameter increases [10].

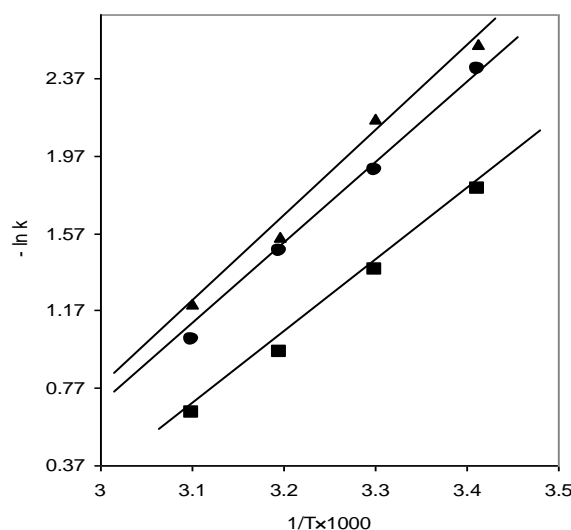


Fig.(4) Plots of $\ln k$ versus $1/T$ using different diluents : ▲ kerosene, ● toluene and ■ LAB+BTX, diameter drop= 0.25cm, [U(IV)] initial= 1M, [HCl]= 4M.

Fig.(4) Shows a plot of $(-\ln k)$ versus $(1/T)$ using initial aqueous uranium concentration of 1M, 4M HCl and 30% TBP with different diluents.

The plot shows linear relationship between $(-\ln k)$ and $(1/T)$.

The dependence of rate constant on temperature can be expressed according to Arrhenius equation:

$$K = A_e^{-E_a/RT}$$

Where :

K = Rate constant

A = Pre-exponential factor (Mathematically, A is the rate constant at infinite temperature K_∞)

From Arrhenius expression, the activation energies for U(IV) in HCl-TBP system in different diluents were calculated and the results are shown in Table (2).

Table (2)
The values of the activation energies for U(IV) in HCl-TBP system in different diluents .

Diluents	E_a (kJ/ mol)
LAB+BTX	31.175
Toluene	35.49
Kerosene	37.02

The activation energy of U(IV) extraction in the concerned diluents increases in the following sequence :

(LAB + BTX) < Toluene < Kerosene .

Consequently the nature of diluents influence the rate constant of extraction which increased in the order:

Kerosene < Toluene < (LAB + BTX).

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تم تطبيق تقنية السقوط الحر للقطرة في دراسة حركية انتقال كتلة اليورانيوم الرباعي في نظام الاستخلاص المذيب المتكون من حامض الهيدروكلوريك و ٣٠ % ثلاثي بيوتيل الفوسفيت (TBP) وباستخدام مذيبات مختلفة مثل الكيروسين، التولوين والمزيج (LAB+BTX) وهو مزيج متساوي الحجمان من كلا من الكيل البنزين المستقيم (LAB) والمزيج المتساوي الحجم المتكون من البنزين والتولوين والزليلين (BTX) ، وعند تراكيز مائية مختلفة من حامض الهيدروكلوريك تتراوح بين (3.4- 7.2M) ، ويتركز ابتدائي لليورانيوم يساوي (1M) .

لقد وجد بأن معدل سرعة الانتقال لليورانيوم الرباعي يزداد بزيادة تركيز المحلول المائي لحامض الهيدروكلوريك، وكذلك بزيادة حجم القطرة .

فضلا على ذلك لقد أظهرت نتائج البحث اختلافا في طاقة التنشيط (Ea) نتيجة لطبيعة المذيب المستخدم ، حيث تزداد الطاقة وفق التعاقب :

الكيروسين < التولوين < (LAB +BTX) .

كما وجد بأن لطبيعة المذيب وخواصه الفيزيائية تأثيرا مباشرا على ثابت معدل سرعة الانتقال في الاستخلاص المذيبي لليورانيوم الرباعي والذي يزداد حسب التعاقب :
LAB+BTX < التولوين < الكيروسين.