Mechanism of Extraction of Hexavalent Uranium from Alkaline Medium by Aliquat-336/Kerosene Solution

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The kinetics of extraction of uranium(VI) from alkaline carbonate medium by tricaprylmonomethylammonium chloride (Aliquat-336) in kerosene has been investigated using a stirred Lewis cell. The effects of different parameters affecting the extraction rate, such as hydrogen ion, carbonate, hydroxide, Aliquat-336, U(VI) concentrations as well as temperature, were separately studied and a rate equation was deduced. The extraction process was found to be governed by chemical reaction in the bulk phase rather than at the interface.

1. Introduction

Based on the high tendency of uranium to form soluble carbonate complexes in alkaline medium,[1, 2] an approach to alkaline dissolution of irradiated uranium was introduced by Ali et al.[3] The proposed process, based on nuclear fuel recycling in a system containing carbonate solution, relies on the solubility of UO_2 in the carbonate medium containing oxidizing agents followed by uptake using basic Bio-Rex 5 exchanger.

On the other hand, although uranium ores can be leached by several solutions to solubilize uranium, only sulfuric acid or sodium carbonate has been practiced. The alkaline digestion method is generally preferred, not only for its simplicity and economic reasons, but also for the fact that the resulting sodium phosphate may be used in the industry of fertilizers.[4] With the alkaline leach, development of extraction systems capable of extraction of uranium in the presence of high salt content at the elevated pH is of great interest. In this context, the amine extraction technique is particularly important since it functions efficiently in strong acid solution and even in alkaline medium with quaternary ammonium ion (e.g. tricaprylmonomethylammonium chloride, Aliquat-336).[5] In this concern, Landgren[6] used Aliquat-336 to investigate the extraction behaviour of several elements, such as Sc, Fe, Zr, some lanthanides, and some actinides, and nitric acid and reported that Aliquat-336 shows high extraction for tetravalent elements and anions: the extraction of multivalent cations was found to decrease in the order $M^{4+} > MO_2^{2+} > M^{3+}$. A selective method has been developed[7] for extraction chromatographic studies of U(VI) with Aliquat-336 (liquid anion exchanger) coated on silica gel as a stationary phase. Quantitative extraction of U(VI) has been achieved at 1.25 – 4 M HCl; U(VI) has been separated from the binary, ternary and quaternary mixture of various metal ions.

The knowledge of the mass transfer rate and mechanism of extraction offered by the kinetic investigations is of major importance for the optimization and control of the extraction process. Tianlin et al.[8] studied the extraction kinetics of uranium (VI) with the binary extractant system of trioctylamine and tri-n-octylphosphine oxide in n-heptane from sulphuric acid media using stationary interface stirring cell at 298 K. The reported synergistic mechanism is controlled by a two step continuous reaction at the interface. Awwad et al.[9]

investigated the kinetics of extraction of U(VI) and Th(IV) from nitric acid solution by tributylphosphate and Cyanex-921 in kerosene using single drop technique. The extraction rate equations for both elements have been deduced, compared and discussed in terms of metal ion, nitric acid, and extractant concentrations.

The present work is directed to investigate the kinetics of uranium extraction from alkaline carbonate medium by Aliquat-336 in kerosene in order to get information on the factors affecting the extraction rate of U(VI) in this system and to propose a mechanism describing the extraction process.

2. Experimental

Chemicals and Reagents. Uranyl nitrate of analytical reagent grade (AR) was a Fluka product, while sodium carbonate and hydrogen peroxide were obtained from Winlab. Aliquat-336 and sodium hydroxide were Merck products. Kerosene (non aromatic) was supplied by Misr Petrol Ltd., Egypt, while 1-octanol was obtained from BDH.

Procedure. Aqueous solution was prepared by addition of oxalic acid to the solution of uranyl nitrate in order to precipitate uranyl oxalate. The precipitate was separated, dried, and heated at 850˚C for eight hours to convert the uranyl oxalate into uranium oxide (U_3O_8). An exact weight of U_3O_8 was dissolved in alkaline carbonate solution composed of 12% (1 M) Na_2CO_3, 15% (1 M) NaOH and 10% (30%) H_2O_2 to form 0.005 M uranium solution. This mixture was heated up to 60˚C with stirring to complete the dissolution process. The concentration of uranium in the aqueous alkaline solution was spectrophotometrically determined by measuring its maximum absorbance at 360 nm using a Shimadzu double beam recording spectrophotometer model 160 A.

Organic solution was composed of Aliquat-336 (5.0 vol%) dissolved in kerosene containing 5.0 vol% of 1-octanol as modifier in order to prevent the formation of a third phase.[2] This produced 0.1 M solution with respect to Aliquat-336.

In the kinetic experiments, the concentrations of Aliquat-336, U(VI), sodium carbonate, and sodium hydroxide were fixed at 0.1 M, 0.005 M, 0.12 M, and 0.15 M, respectively unless their concentrations were otherwise stated. The temperature was fixed at 25 ± 0.1˚C by using a Julabo (Germany) circulator connected to a stirred Lewis cell. The cell description and general procedures were previously described.[10]

A stirring rate of 250 rpm was chosen for the kinetic investigations performed in this work. The plots of $\ln(C_{eq}-C)$ versus time (t) always yielded straight lines indicating a first-order

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reaction, where C_{eq} and C represent the concentration of U(VI) in the organic phase at equilibrium and that at time t, respectively. The observed rate constants (k_{obs}) were calculated from the respective slopes of these straight lines.

The surface tension at the Aliquat-336-kerosene/aqueous alkaline carbonate interface was measured by Du Nouy ring method using a CsC Du Nouy Tensiometer model 70545.
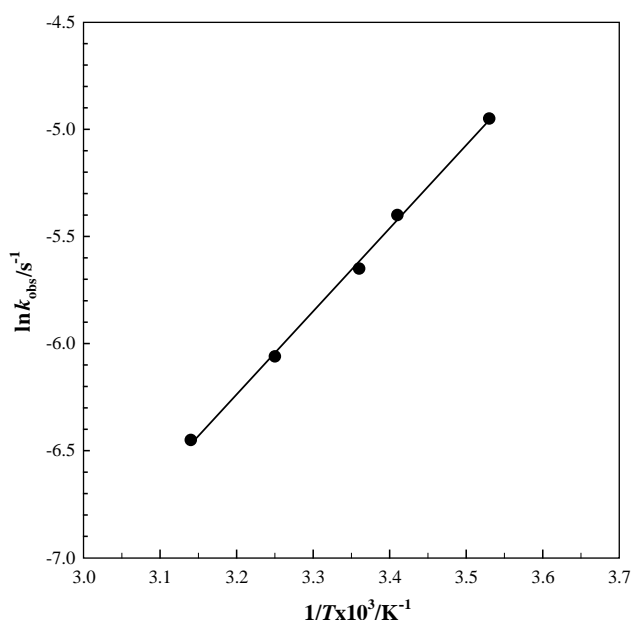
3. Results and Discussion

In stirred Lewis cell technique, the controlling process is determined from the effect of the stirring speed as well as the effect of temperature. When the extraction is controlled by diffusion, the rate of extraction increases with the increase in the stirring rate, while there is no effect on the extraction rate when it is governed by chemical reaction.[11] The effect of stirring rate on the rate of extraction of U(VI) by Aliquat-336 in kerosene from alkaline medium was studied in the stirring range 100 – 400 rpm and a plateau region is obtained in the range 200 – 300 rpm. As the stirring rate used in the present work is fixed at 250 rpm which lies in this plateau region, the extraction process is assumed to be mainly controlled by chemical reactions.

The effect of temperature on the rate of extraction of systems governed by diffusion is less pronounced than that controlled by chemical reactions since the activation energy in the former case does not usually exceed 20.9 kJ mol^{-1}.[12] In the present work, the effect of temperature on the extraction rate of U(VI) by Aliquat-336 was investigated in the range 10 – 45°C. The plot of the calculated values of ln k_{obs} against the corresponding values of $1/T$, in Figure 1, shows a linear decrease in ln k_{obs} reciprocally with the increase in temperature, which obeys the Arrhenius equation $k_{obs} = Ae^{-E/RT}$ (T is the absolute temperature and R is the universal gas constant and A is a constant). The activation energy (E) calculated from the slope of this line was found to be 32.26 kJ mol^{-1}, which verifies that the extraction rate of U(VI) in the investigated system is controlled by chemical reaction taking place either in the bulk phase or at the interface.

The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) of the investigated system were calculated to be 29.78 kJ mol^{-1} and -57.2 kJ mol^{-1} K^{-1}, respectively.

The effect of the interfacial area on the extraction rate was studied to identify whether the system is controlled by chemical reaction taking place in the bulk phase or at the interface. The rate of extraction increases linearly with the increase in the specific interfacial area ($\bar{a}$) (where $\bar{a}$ = interfacial area (Q) / volume of the phase (V)) in systems when it is controlled by chemical reaction at the interface, while there is no effect of $\bar{a}$ when the controlling reaction takes place in the bulk phase.[13] In this concern, the effect of varying the specific interfacial area on the rate of extraction of U(VI) was studied in the range 6.6 – 15.9 cm^2 by using different cells at V = 30 mL for each phase, keeping all other experimental conditions constant. The plot of k_{obs} against the corresponding specific interfacial area ($\bar{a}$) gave constant values of the reaction rate constant with increasing $\bar{a}$, indicating that the extraction rate of U(VI) is independent of the surface area between the aqueous and organic phases (Figure 2). This means that the rate controlling reaction takes place in the bulk phase rather than at the interface.

The interfacial tension measurements are particularly important because they can provide useful information on the interfacial properties of the extractant. As octanol was always added to Aliquat-336-kerosene solution, interfacial tension was measured in the presence of this modifier. The interfacial tension measurements were carried out at different Aliquat-336 concentrations in the range 0.02 – 0.14 M in kerosene containing a certain amount of octanol (5.0 vol.%). In spite of low distribution of Aliquat-336 in aqueous phase,[2] the results of the interfacial measurements show that, under the experimental conditions in the present study, the organic/aqueous interfacial tension remains constant independent of the extractant concentration (Figure 3). This indicates that Aliquat-336 is not adsorbed at the interface but lies mainly in the organic phase and verifies that the rate of U(VI) extraction is controlled by chemical reaction in the bulk phase rather than at the interface.

The effect of Aliquat-336 concentration on the extraction rate of U(VI) in the system was studied in the range 0.06 – 0.14 M. The metal extraction rate was found to increase linearly with the increase in Aliquat-336 concentration (slope = 1). The increase in U(VI) concentration from 0.002 to 0.01 M had almost no effect on the extraction rate. The effects of carbonate and hydroxide concentrations in the respective
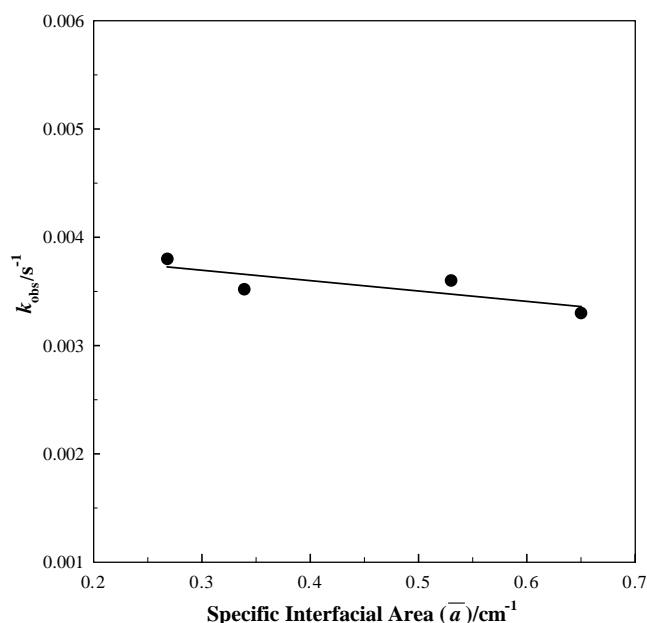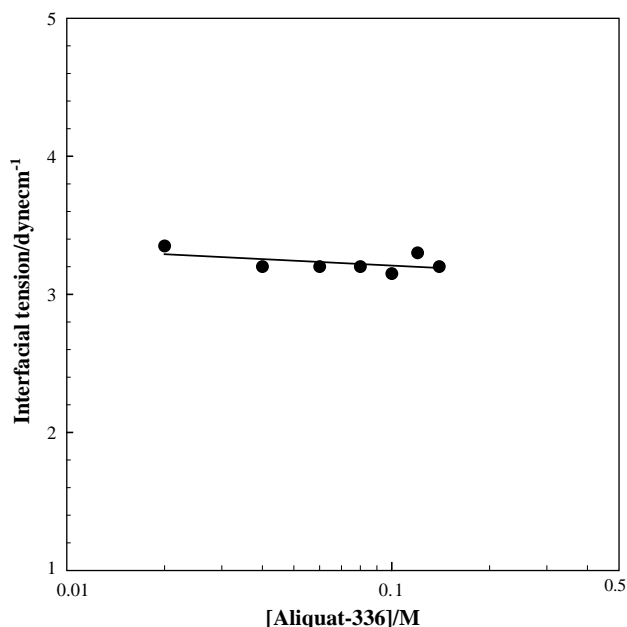

Figure 1. Effect of temperature on the rate of extraction of U(VI) by Aliquat-336 in kerosene from alkaline carbonate medium.
[U(VI)] = 0.005 M, [Aliquat-336] = 0.1 M,
Stirring rate = 250 rpm.

Figure 2. Effect of specific interfacial area ($\bar{a}$) on the rate of extraction of U(VI) by Aliquat-336 in kerosene from alkaline carbonate medium.
[U(VI)] = 0.005 M, [Aliquat-336] = 0.1 M,
Stirring rate = 250 rpm, T = 25°C, $V_{aq.}$ = $V_{org.}$ = 30 mL.

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ranges of 0.02 – 0.15 M and 0.025 – 0.20 M were examined and are almost nothing until their concentrations of 0.1 M and 0.12 M, respectively. However, afterwards, the extraction rate constant drastically decreased with increasing the carbonate and hydroxide concentrations giving straight lines with slopes = -1 for each case. The drastic decreasing effect of increasing carbonate in the medium may be explained by the formation of higher uranium carbonate complexes, such as $[UO_2(CO_3)_3]^{4-}$, which decrease the extraction of the main extracted species, $[UO_2(CO_3)_2]^{2-}$;[14] the decreasing effect caused by the increase in hydroxide concentration may be related to the increase in pH which in turn decreases the extraction process.[14]

All data above-mentioned, the slopes of the log – log relations between k_{obs} and [Aliquat-336], [U(VI)], $[CO_3^{2-}]$, and $[OH^-]$, are given together in Figure 4. This figure indicates that the reaction is first order dependent on Aliquat-336 concentration, nearly zero order on U(VI) concentration, and inverse first order on carbonate and hydroxide concentrations.

As the predominant uranium species in alkaline carbonate medium is considered to be $UO_2(CO_3)_3^{4-}$,[15, 16] the main extracted uranium species by Aliquat-336 is supposed to be $UO_2(CO_3)_2 \cdot 2R$ (R: Aliquat-336 molecule).[14] Based on the kinetic results mentioned above, obtained under the employed experimental conditions, the mechanism of U(VI) distribution between alkaline medium and Aliquat-336 in kerosene solution is expected to proceed through the following steps:

1. Distribution of Aliquat-336 (R^+OH^-) between the organic and aqueous phases.

$$\overline{R^+OH^-} \underset{}{\overset{K_D}{\rightleftharpoons}} R^+OH^- \qquad K_D = \frac{\overline{[R^+OH^-]}}{[R^+OH^-]} \qquad (1)$$
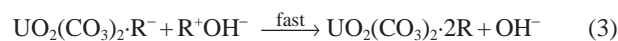
Where, bars refer to the organic phase species, K_D is the distribution constant of R^+OH^-.

2. Slow reaction between the predominant uranium tricarbonate complex and one R^+OH^- in the aqueous phase with the release of one hydroxide and one carbonate.

$$UO_2(CO_3)_3^{4-} + R^+OH^- \xrightarrow[k_1]{slow} UO_2(CO_3)_2 \cdot R^- + OH^- + CO_3^{2-} \quad (2)$$

3. Fast addition of another R^+OH^- molecule to give neutral uranium species with the release of one hydroxide ion.

$$UO_2(CO_3)_2 \cdot R^- + R^+OH^- \xrightarrow{fast} UO_2(CO_3)_2 \cdot 2R + OH^- \qquad (3)$$

4. Fast transfer of the formed neutral uranium species to the organic phase.

$$UO_2(CO_3)_2 \cdot 2R \xrightarrow{fast} \overline{UO_2(CO_3)_2 \cdot 2R} \qquad (4)$$
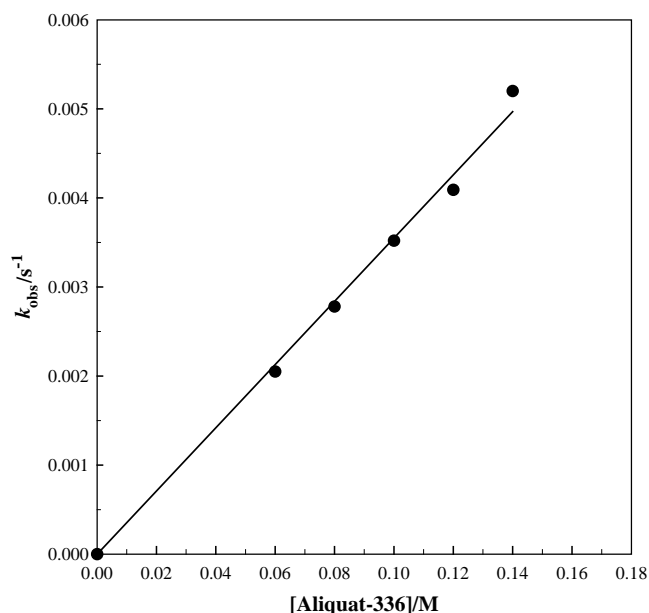
Since step (2) is assumed to be the rate-determining step, therefore, the rate of extraction is given by the following equation:

$$\text{Rate} = \frac{-d[UO_2(CO_3)_3^{4-}]}{dt} = k_{obs}[UO_2(CO_3)_3^{4-}] \qquad (5)$$

$$= k_1[UO_2(CO_3)_3^{4-}][R^+OH^-], \qquad (6)$$

where k_1 is the rate constant of the slow reaction given in eq 2, and

$$k_{obs} = \frac{k_1}{K_D}\overline{[R^+OH^-]}. \qquad (7)$$

Figure 3. Effect of interfacial tension of $\overline{R^+OH^-}$ on the alkaline carbonate/kerosene interface.
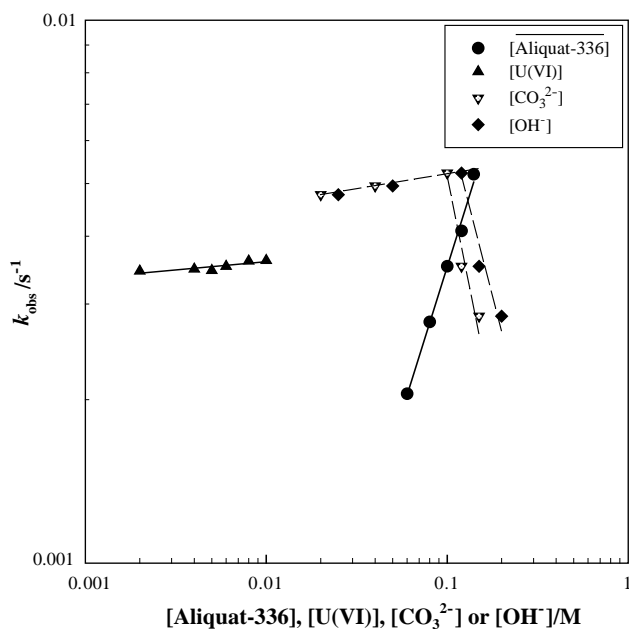
Figure 4. Effect of $\overline{R^+OH^-}$, U(VI), CO_3^{2-} or OH^- concentration on the extraction rate of U(VI) by Aliquat-336 in kerosene from alkaline carbonate medium.
Stirring Rate = 250 rpm, $T = 25°C$.

Figure 5. Relation between the reaction rate constant (k_{obs}) and $\overline{[R^+OH^-]}$ for the extraction of uranium from alkaline carbonate medium.

Equation 7 is an equation of a straight line passing through the origin. The plot of the experimental values of k_{obs} obtained at different initial extractant concentrations $\overline{[R^+OH^-]}$, shown in Figure 3, yields a straight line passing through the origin with slope = k_1/K_D, which verifies eq 7 and supports the proposed mechanism.

4. Conclusions

The extraction rate constant was found to decrease with increasing temperature. The activation energy obtained was found to be 32.6 kJ mol^{-1}, which indicates that the rate of uranium extraction by Aliquat-336 in kerosene is controlled by chemical reaction.

The extraction rate is independent of interfacial area. Furthermore, the interfacial tension at the alkaline/kerosene interface is constant at different Aliquat-336 concentrations. These verify that the rate of extraction of U(VI) in the system is governed by a chemical reaction taking place in the bulk phase rather than at the interface.

The obtained kinetic results show that the extraction rate of U(VI) by Aliquat-336 from alkaline carbonate medium is accelerated by the increase in the extractant concentration, but in contrast, slowed down by the increase in the concentrations of carbonate and hydroxide in their high concentration ranges.

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