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# Determination of Stability Constant of Uranium Complex Formation In The Presence Of Leucine and Isoleucine

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***Abstract:*** *In this work, Calculation of the formation constant of uranium (VI) complexes with leucine and isuleusine has been determined in the PH renges 1 to 3.5 and ionic strength in 0.1 mol/dm$^3$ sodium pherchlorate at 25+0.1 ℃ and wave lenghth of 250 to 285 nm (distance of 5 nm each) by potentiometry and spectrophotometric methods.The average values of logarithms of the stability constants for complexes of $UO_2^{+2}$ with Leucine for models of MHL and (HL)$_2$is equal to 2.76 and 5.12, respectively and for complexes of $UO_2^{+2}$ with isoleucine, for models of MHL and M(HL)$_2$is equal to 2.26 and 4.62 respectively.*
***Keywords:*** *Uranium (VI), leucine, isoleucine, spectrophotometry.*

## I. Introduction

Primarily the transition metal chemistryis related to coordination compoundschemistry.Nowadays coordinationcompounds thatcalled "complexes" have very important role in our daily lives.Coordination compounds or metal complexes arecontaining a central atom or ion that is surrounded by a cluster of ions or molecules [1,3].According to chargetotal of the central atom and ions and molecules that surrounded them, divide them into three categories cationic, anionic and non-ionic. These compoundsplay a major role in chemical and biological systems [4]. Complex in which the electrons can have a significant role in the formation of chemical bondcalled donor-recipient complex.Properties of a metal ion complex in solution are depends on the nature of the ligands that is surrounded the metal.Complex stability,predict the factors contributing to the stability of metal complexes andso far a large number of complex stability constant has been determined [2].Complex formation creates the changes in physicochemical properties of solutions.Basically, any parameters to be changed as a result of complex formation, used to study of the complex structure and calculation of formation constant [3].Various methods are available to determine the complex stability constants,the existing experimental methods for determining of stability constants can benoted to polarimetric techniques, potentiometric, colorimetric [6].

Effective factorsin the complex formation are includes: (a) Ligand is the most important factor to complex formation. Type of the ligand, ligand size, and number of the ligand are very affect to the stability of complexes. (b) The second factor that is effective in complex formation is a central metal[2,4].

In this work fromUranyl acetate is used instead of uranium (VI), also to ligand formation used from leucine and isoleucine. Both Leucine and isoleucine are an amino acid.Leucine amino acid (abbreviated as Leu or L) was discovered in 1820, andits chemical formula is C6H13NO2.This amino acidalong with eight other amino acids has hydrophobic properties.Scientists have proved that thechain amino acidswereproductenergy during exercise [5,7].It also led to the development of the synthesis of specific proteins.Leucineis applies anti-catabolic effects on individuals in the regime [5].Lucien toxicity is seen in disease (MSUD),that it is caused the frenzy, nervousness, backwardness and can be life-threatening. Also Isoleucine is one of the essential amino acids for humans,whichthere amounts to less than other amino acids in proteins.Essentialamino acids are called to amino acids that the body alone cannot produce them and must be obtained through food [4].

## II. Experimental Method

In this study to determination of the stability constant of complex formation of uranium (VI) with leucine and isoleucine, spectrophotometric titration method is used.Measuring the stability constant of a complex that is associated with protonation, has two main components are: (a) protonation of ligand, (b) stability of complex. With knowing the constant of ligand protonation can be calculate the stability constants of complex systems composed according to available balance relations.

### 2.1 chemical materials

All of the materials include Perchloric acid with a purity of 60%, Sodium perchlorate (98%), solution of sodium hydroxide-tetrazole (1M), Leucine and isoleucineamino acid (99%), and Uranyl acetate (99%), made and product by Merck.Also in all of the test stages is used from bidistilled water with a 1.5 ± 0.1 Ω conductivity.

**2.2 Devices**

In this work, a pH meter to measure of -log [H +] is used that its type is pHM 960PreCise.Determination of absorption is performed by spectrophotometer UV PerkinElmer Lambda25 brands made in America and has been equipped with computers.Spectrophotometer cells with a diameter of 10 mm made of quartz.The type of warm bath was Optima 740.Type ofBalance Used in this work is Sartorius CP 1248 and made in Germany.

## III. Results And Discussion

Before the experiment began, early solution were prepared which contains titrand and titrant (titrator)solution. Then to determination of the stability constant of complex formation of uranium (VI) byspectrophotometric titration method,pH and absorption at different wavelengths were measured for both systems simultaneously,that these work was performed inspace of 250 nm to 285 nm every 5 second for Uranyl acetate system in the present of leucine and isoleucine.It should be noted that the solution containing ligand was prepared fresh daily and the solution temperature is kept constant by the thermostat at ℃25. The titration was repeated at least 3 times andthe average results of them were recorded and used.

Logarithm values of $\beta_{MHL}$, $\beta_{M(HL)2}$, $k_{MHL}$, $k_{M(HL)2}$ and absorption coefficient of complex $Uo_2^{+2}$ with leucine and izoleucine at a wavelength of 270 nm and temperatures ℃25 and ionic strength of sodium pherchlorate equal 0.1 M have been recorde in Table (1,2 ) respectively. Also the protonation constants of leucine and isoleucine amino acids are shown in Table (3). Chart of mole fraction change vs pH for uranium (VI) system with the leucine amino acid was plotted at a wavelength of 270 nm (figure.1). This chart shows the ionic species $UO_2^{+2}$ has been spent by increasing the pH, and mole fraction of $UO_2HL^+$ increased with increasing of the pH, and reached maximum value when the pH equal about to 6/2 and then decreased. The values of second type of complex $UO_2 (HL)_2$ as the first type rises by increasing the pH, and this increase will continue until the final pH. The experimental and calculated absorption values are compared with together and that is shown in Figure (2). Chart values (2) shows that both the $A_{cal}$ and $A_{exp}$ diagram vs PH were coincide with very few errors, that it is shows the experimental results too close to reality results.

Because uranium metal has an absorption, the graph started from absorption 0.2 and pH 1.288, then the absorption were reduced by added of titrant, gradually.

Chart of mole fraction change vs pH for uranium (VI) system with the Izoleucine amino acid was plotted at a wavelength of 270 nm (figure.3). This chart suggests an explanation that $UO_2^{+2}$ has been spent with increasing of pH, as well as the species of $UO_2 (HL)_2$ and $UO_2HL^+$ were product with increasing pH and titration starting. Chart (4) shows the comparing of $A_{exp}$ and $A_{cal}$ charts vs pH, that both the $A_{cal}$ and $A_{exp}$ diagram vs PH were coincide with very few errors, that it is shows the experimental results too close to reality results. Because uranium metal has an absorption, the graph started from absorption 0.2078 and pH 1.0288, then the absorption were reduced by added of titrant, gradually because metal ions are consumed gradually and species-complex is formed.

To calculate the protonation constants, the computer simulation is used,for this purpose, two reactions are considered to amino acids:

**1)** $H_2L \leftrightarrow HL^- + H^+$ **(1)**

**2)** $HL^- \leftrightarrow L^{2-} + H^+$ **(2)**

According to the Mass law, relationship ofequilibrium constant $k_1$ and $k_2$ with the protonation is as follows:

$K_1 = [HL^-][H^+]/[H_2L]$ **(3)**

$K_2 = [L^{2-}][H^+]/[HL^-]$ **(4)**

Therefore, the total concentration of the ligand can be written as follows:

$C_L = [L^{2-}] + [HL^-] / [H_2L]$ **(5)**

Using the Beer-Lambert law can be achieved so relationship between absorption coefficients and total ligand concentration and equilibriumconstants:

$A = \varepsilon\, b\, c$ **(6)**

$A_{cal} = \varepsilon_{H2L}[H_2L] + = \varepsilon_{HL}[HL] + \varepsilon_L[L^{2-}]$ **(7)**

In the spectrophotometric measurements, total absorptionof solution is obtained from the following equation:

$$[H2L] = \frac{C_L[H^+]^2}{[H^+]^2 + L[H^+]K_1 + K_1K_2} \quad (8)$$

This equation is an equation with three unknowns that it can be solved using the softwareMathematical.

If we assume that $[H^+]^2 + [H^+]K_1 + K_1K_2 = \beta$ in this case, we have:

$[H_2L] = C_L[H^+]K_1/\beta$ (9)
$[L^{2-}] = C_L K_1 K_2/\beta$ (10)

After which the relationship between absorption coefficients and total ligand concentration and equilibrium constants can be achieved by used of computer software, then by using of absorption obtained from spectrophotometry, can be calculate the molar absorption coefficients and equilibrium constant.

To calculate the stability constants of complexes MHL and M $(HL)_2$ according to the following equilibrium:

$M+H_2L \leftrightarrow H^+ + MHL$ (11)
$MHL+H_2L \leftrightarrow M(HL)_2+H^+$ (12)

And according to the mass balance we have:

$K_1 = [H^+][MHL]_P/[M][H_2L]_{f1}$ (13)
$K2 = [H^+][MHL]_2/[M][H_2L]_{f2}$ (14)
$C_M = [M] + [[MHL]_P + [M(HL)_2]$ (15)
$C_L = [MHL] = 2[M(HL)_2] + [H_2L]_{f1} + [H2L]_{f2}$ (16)
$[MHL]_P = [M(HL)_2] + [MHL]$ (17)

In the above equations, $C_L$ and$C_M$ values represent the total concentration of ligand and complex respectivelythat are obtained from experimental methods, also $H^+$ concentration obtained from the equation $[H^+] = 10^{-PH}$.The values of [M], $[MHL]_P$,$[H_2L]_{f1}$, $[H_2L]_{f2}$, $[M(HL)_2]$ and [MHL] are unknown that are calculated by a computer program, then theobtained values are inserted in the following equation:

$Acal = \varepsilon_0[M] + \varepsilon_{MHL}[MHL] + \varepsilon_{M(HL)_2}[M(HL)_2]$ (18)

Finally, the values of theabsorption coefficients of MHL complex ($\varepsilon_{MHL}$), absorption coefficients of $M(HL)_2$ complex ($\varepsilon_{M(HL)_2}$ , formation constant of MHL complex ($K_{MHL}$), formation constant of $M(HL)_2$ complex ($K_{M(HL)_2}$ were calculated by used of fittingoperation (processing).

Complex stability constants are defined as follows:

$M+L \leftrightarrow ML$ (19)
$ML+L \leftrightarrow ML_2$ (20)
$K_{ML}=[ML]/[M][L]$ (21)
$K_{ML2}=[ML_2]/[ML][L]$ (22)

The combination of relations (3) and (13), Equation (23) is achieved:

$\beta_{ML}=K_1^* K_{H1}$ (23)

And with combination of relations (3) and (14), Equation (24) is achieved:

$\beta_{ML2}= K_2^* K_{H2}$ (24)

## IV. Conclusion

The aim of this study was to determine the stability constant of complex formation of uranium (VI) with the leucine and isoleucine amino acids in the acidic environment has been using spectrophotometric methods,and this operationis based on the relationship A = f (pH),also pH and absorptionfor $UO_2^{+2}$ system with leucine and isoleucinewere measured at a wavelength of 250 to 285 (every 5 nm),all of the measurements has been done in constant ionic strength of 1.0 M sodium perchlorate and a temperature of 25 ° C.That in finally the stability constants of complexes $UO_2^{+2}$ with amino acids were calculated.

The formation of complexes indicates that uranium (VI) creates the complexes with leucine and isoleucine by molar ratio of 1: 1 and 2: 1 (the ratio of metal to ligand) as species of $UO^2HL^+$ and $UO_2(HL)_2$ .

Effective internal factors of thecomplexes stability constant is including the chemical properties of metal ion, spatial effect and the effect of ligands,due to the complex $UO_2^{+2}$ for both is same the spatial effect and the effect of the ligand can have an impact on the stability constant of complex.And external factors such as temperature, solvent and ionic strength, etc., can not have an impact on results,because, themwere constant in during of the tests.

Complex $M_xH_yL_z^{(nx+y-z)+}$ is composed fromcharacterswith stoichiometry Z, Y and X,that M and L, whererepresented tometal ions and ligands respectively.

Stability constantor protonation were determined, that is defined by the following expressions:

$xM^{+n}+yH^++zL^- \leftrightarrow M_xH_yL_z^{(nx+y-z)+}$
$\beta_{xyz}= [M_xH_yL_z^{(nx+y-z)+}]/([M^{+n}]^x[H^+]^y[L^-]^z)$

Using appropriate computer programs and gain empirical data, the stability constantis calculated for different stoichiometric moles.

In aqueous solution, the ligands is formed as anionic ($L^-$), dual ion (HL), and cationic $(H2L)^+$that in this work the species of HL is dominant in acidic environment.

Stoichiometric models of $UO_2L$, $UO_2HL^+$, $UO_2HL_2$, $UO_2H_3L_2^{+2}$ , $UO_2H_3L_3^+$and $UO_2H_4L_4^+$rejected spontaneously by a computer program,and the final selectiontakes place based on the two type of fitting both graphical and numerical fitting, that selected models to complexuranium (VL) with the amino acid is two models $UO_2HL_2$and $UO_2HL^+$ .

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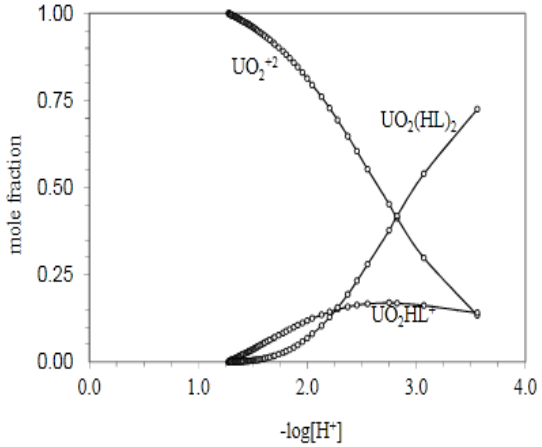


**Figure1**

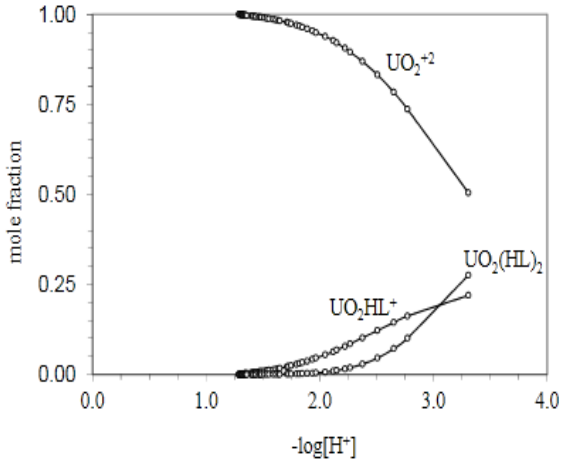


**Figure 3**

Figure (1) & (3). Chart of mole fraction change vs pH for uranium (VI) system with the leucine and isoleucine amino acids respectively at a wavelength of 270 nm and temperatures ℃25 and ionic strength of sodium pherchlorate equal 0.1 M

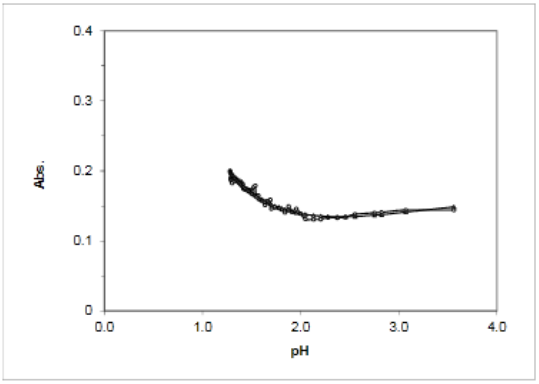


**Figure (2)**

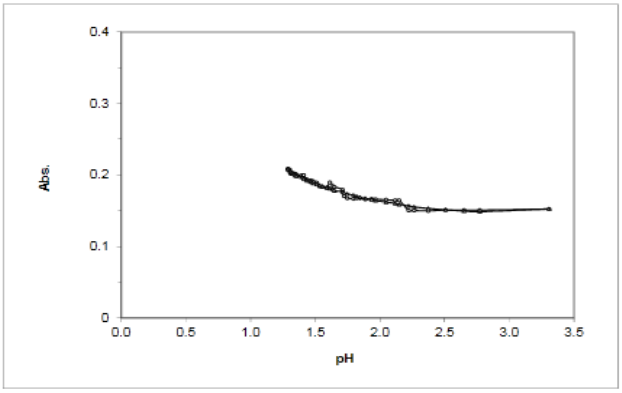


**Figure (4)**

Figure (2) & (4). The comparison of experimental and calculated absorption values with together for complexes system with leucine and isoleucine respectively.

**Table (1)** Logarithm values of $\beta_{MHL}$, $\beta_{M(HL)2}$, $k_{MHL}$, $k_{M(HL)2}$ and absorption coefficient of complex $Uo_2^{+2}$ with leucine and at a wavelength of 270 nm and temperatures ℃25 and ionic strength of sodium perchlorate equal 0.1 M

| $\lambda$ | $logK_{MLH}$ | $logK_{M(HL)_2}$ | $log\beta_{MLH}$ | $log\beta_{M(HL)_2}$ | $E_{MHL}$ | $E_{M(HL)_2}$ |
|---|---|---|---|---|---|---|
| 270 | 0.4 | 0.83 | 2.76 | 5.12 | 70.44 | 251.64 |

**Table (2)** Logarithm values of $\beta_{MHL}$, $\beta_{M(HL)2}$, $k_{MHL}$, $k_{M(HL)2}$ and absorption coefficient of complex $Uo_2^{+2}$ with izoleucine and at a wavelength of 270 nm and temperatures ℃25 and ionic strength of sodium perchlorate equal0.1 M

| $\lambda$ | $logK_{MLH}$ | $logK_{M(HL)_2}$ | $log\beta_{MLH}$ | $log\beta_{M(HL)_2}$ | $E_{MHL}$ | $E_{M(HL)_2}$ |
|---|---|---|---|---|---|---|
| 270 | -0.1 | 0.19 | 2.26 | 4.62 | 81.15 | 4.26 |

**Table (3)** Protonation constants of leucine and isoleucine amino acids

| amino acids | $K_1$ | $K_2$ |
|---|---|---|
| leucine | 4.37 E -03 | 2.51 E -10 |
| isoleucine | 4.37 E -03 | 2.09 E -10 |