SPECTROSCOPIC BEHAVIOUR OF TRIETHYLENE-TETRAAMINEHEXAACETIC ACID WITH TETRA AND HEXAVALENT URANIUM IN SOLUTION

By

MOHAMED B. HAFEZ, WAFAA S. HEGAZI[#] and NABIL HAFEZ

Hot Laboratory Center, Atomic Energy Establishment,
Cairo- Egypt.

ABSTRACT

The interaction between triethylenetetraaminehexaacetic acid (TTHA) and tetra and hexavalent uranium is investigated. Evidence is given for the formation of a stable and soluble 1:1 tetravalent uranium chelate. An insoluble 2:1 chelate between uranyl ions and TTHA is formed between pH 2 and 4. Also two soluble 1:1 and 2:1 chelates are formed. Stability constants (log K) of the soluble complexes were calculated to be 15 and 11.8 respectively.

INTRODUCTION

Complex formation between tetra and hexavalent uranium and TTHA has been studied by some workers.[1,2] However, the composition and the stability of the formed complexes were not definitely determined. The probable formation of several uranyl-TTHA chelates

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University College for Girls, Department of Chemistry, Ain Shams University, Cairo, Egypt.

with different compositions, in the pH range 2–8 was previously reported.[3] Other studies,[4] at low pH, showed that uranyl ions react with TTHA to form only a mononuclear chelate, whose stability varies with the pH and the concentration of the chelating agent. In view of the contradictions in the published data on the uranyl-TTHA chelates, a detailed quantitative study of the equilibria involved in the interaction of tetra and hexavalent uranium ions with TTHA, over a wide range of pH and TTHA concentrations, is undertaken in the present work.

EXPERIMENTAL AND CALCULATIONS

All chemicals used were Analar grade. Tetravalent uranium was freshly prepared by reducing uranyl ions with nascent hydrogen gas using orthochloroplatinic acid as a catalyst.[5] The chelate solutions were prepared by mixing solutions of uranyl ions and TTHA in acidic medium, then adjusting the pH of the mixtures by adding carbonate-free sodium hydroxide solution.

pH-measurements were made using a Pye Unicam Model 292 pH-meter. Spectrophotometric studies were carried out with the aid of a Beckman DU-spectrophotometer, using 1 cm quartz cells.

Formation constants of the chelates were evaluated,[6] and accordingly, the stability constants (log K) were then calculated.[7,8]

RESULTS AND DISCUSSION

I. Chelation of Tetravalent Uranium (U(IV)):

I.1. Absorption spectra of (U(IV)+TTHA) mixture as a function of pH:

The absorption spectrum of $8x10^{-2}$M U(IV) and $3.2x10^{-1}$M TTHA mixture at pH = 1 is identical with that of free U(IV) ions, with absorption maxima at 458, 532, 618 and 645 nm.[4] In the pH range 2.2 - 9.5 the spectrum exhibits characteristic maxima at 464, 538, 622 and 650 nm (Fig.1). This shows that a U(IV)-TTHA complex is formed momentarily within the pH range 2.2 - 9.5. Between pH 2 and 4 the spectra of the mixture did not change for a long period after preparation. However, at pH $\geq$4.5 the U(IV)-TTHA complex changed gradually with time to U(VI)-TTHA.

I.2. Determination of the composition of the formed chelate:

I.2.a) The mole ratio method:

The concentration of U(IV) was kept constant at $8x10^{-2}$M and the [U(IV)] / [TTHA]ratio was varied between 1.00 / 0.25 and 1/4. The pH of the mixture was maintained at 2.2, and the absorbance was measured at 650 nm.

I.2.b) The continuous variation method:

Different concentrations of U(IV) and TTHA were mixed together such that the total concentration was always $1.6x10^{-2}$M. All the solutions were adjusted at pH 2.2 and the optical denisty measurements were made at 650 nm.

Both of the above methods point to the formation of 1:1 chelate, as can be seen from Figs. 2 a) and 2 b). The value of the stability constant of the complex (log K) was calculated to be 20.7 .

II. Chelation of Hexavalent Uranium (U(VI)):

II.1. Absorption spectra of (U(VI)+TTHA) mixture as a function of pH:

The absorption spectra of $8x10^{-2}$M uranyl ions in 0.2N HCl and that of (U(VI)-TTHA) mixtures at different pH values are given in Fig. 3. It was found that at pH=1.5 the spectrum of the mixture is similar to that of free uranyl ions. In the pH range 2-3 a yellow precipitate is formed indicating the formation of an insoluble compound. Between pH 3.5 and 8 a soluble complex is formed as indicated by the increase in the absorbance with increasing pH. At pH >8 the absorbance decreases with increasing pH and uranyl hydroxide is precipitated.

II.2. Determination of the composition of the chelate:

II.2.a) The mole ratio method:

The absorption spectra of mixtures composed of $8x10^{-2}$M U(VI) and various TTHA concentrations ranging from $8x10^{-3}$ to $8x10^{-1}$M at different pH values are given in Fig.4. An insoluble

2U : 1L complex is formed at a pH range 2-3.5. A soluble 2U : 1L complex is observed at 420 nm in the pH range 4.5 -5.5. Between pH 5.5 and 8 a part of uranyl ions was precipitated indicating that the above mentioned complex does not exist at this pH range. Another soluble 1:1 complex is observed between pH 4.5 and 8. At pH = 8.5, however, the uranyl ions undergo hydrolysis yielding the hydroxide.

II.2.b) The continuous variation method:

The total concentration of (U(VI)-TTHA) solution mixtures was kept at 1.6×10^{-2}M and the pH of each solution was adjusted at 4.5. The optical measurements were recorded at 420 nm, from which the formation of two U(VI)-TTHA complexes of mole ratios 1:1 and 2:1 could be concluded. This is in accordance with the results obtained from the mole ratio method.

The values of the stability constants (log K) were found to be 15.0 and 11.8 for the two complexes respectively.

The competition between the oxygen of the uranyl group and the chelate ligand may be a factor which decreases the stability of the formed complex.[9] Similar instability of uranium complexes was also observed with other liganda such as citrates,[10] amines[11] and other polyaminopolycarboxylic acids.[12]

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المتراكبات الناتجـــة عن ترابـــط ثلاثى ايثيلين رباعى امين سداسى حمض الخليك مع كل من اليورانيوم الرباعى واليورانيوم السداسى التكافـــؤ

محمد بدر الدين حافظ — وفاء صلاح حجازى* — نبيل حافظ
معهـــد بحوث الطاقـة الذرية

تم فى هذا البحث دراسة الترابط بين مشتق الحمض الامينى : ثلاثى ايثيلين رباعى امين سداسى حمض الخليك وبين كل من اليورانيوم رباعى التكافؤ واليورانيوم سداسى التكافؤ لاحتماله تكوين مركبات متراكبة . وقد دلت النتائج على تكوين متراكب ثابت وقابل للذوبان فى الماء بنسبة تركيبية ١ : ١ بين اليورانيوم الرباعى وبين مشتق الحمض الامينى . كذلك اثبتت النتائج تكوين متراكب غير قابل للذوبان بين ايون اليورانيل وبين مشتق الحمض الامينى بنسبة تركيبية ٢ : ١ فى المحاليل ذات الأس الهيدروجينى اكثر من ٢ واقل من (او يساوى) ٤ .

ايضا تم الاستدلال على تكوين متراكبين قابلين للذوبان فى المحلول المائى بنسبة تركيبية ٢ : ١ ، ١ : ١ بين شق اليورانيل ومشتق الحمض الامينى على التتالى . وفى جميع الاحوال تم حساب ثوابت الاتزان للمتراكبات القابلة للذوبان المذكورة أعلاه .

* كلية البنات ـ قسم الكيمياء ـ جامعة عين شمس .

FIGURES

1. Effect of pH on the absorption spectra of (U(IV)+TTHA) mixture; $[U(IV)] = 8\times10^{-2}M$, $[TTHA] = 3.2\times10^{-1}M$; 1) pH = 2.2, 2) pH = 5.5, 3) pH = 7.5, 4) pH = 9.5 and 5) U(IV) only.

2.a) Variation of the absorbance at 650 nm with the mole ratio $[U(IV)] / [TTHA]$ at pH 2.2, $[U(IV)] = 8\times10^{-2}M$,

2.b) Variation of the absorbance at 650 nm for (U(IV)-TTHA) mixtures with mole fraction at pH 2.2, total concentration of the mixtures $1.6\times10^{-2}M$.

3. Effect of pH on the absorption spectra of (U(VI)+TTHA) mixtures; $[U(VI)] = 8\times10^{-2}M$, $[TTHA] = 3.2\times10^{-1}M$.

1) pH = 3.5, 2) pH = 4.5, 3) pH = 5.5, 4) pH = 6.0, 5) pH = 6.5, 6) pH = 7.0, 7) pH = 7.5, 8) pH = 8.0, 9) pH = 9.5 and 10) U(VI) only in 0.2N HCl.

4. Variation of the absorbance at 420 nm with the molar ratio of hexavalent uranium to TTHA; $[U(VI)] = 8\times10^{-2}M$, A) pH = 3.5, B) pH = 4.5, C) pH = 5.5 and D) pH = 7.5.

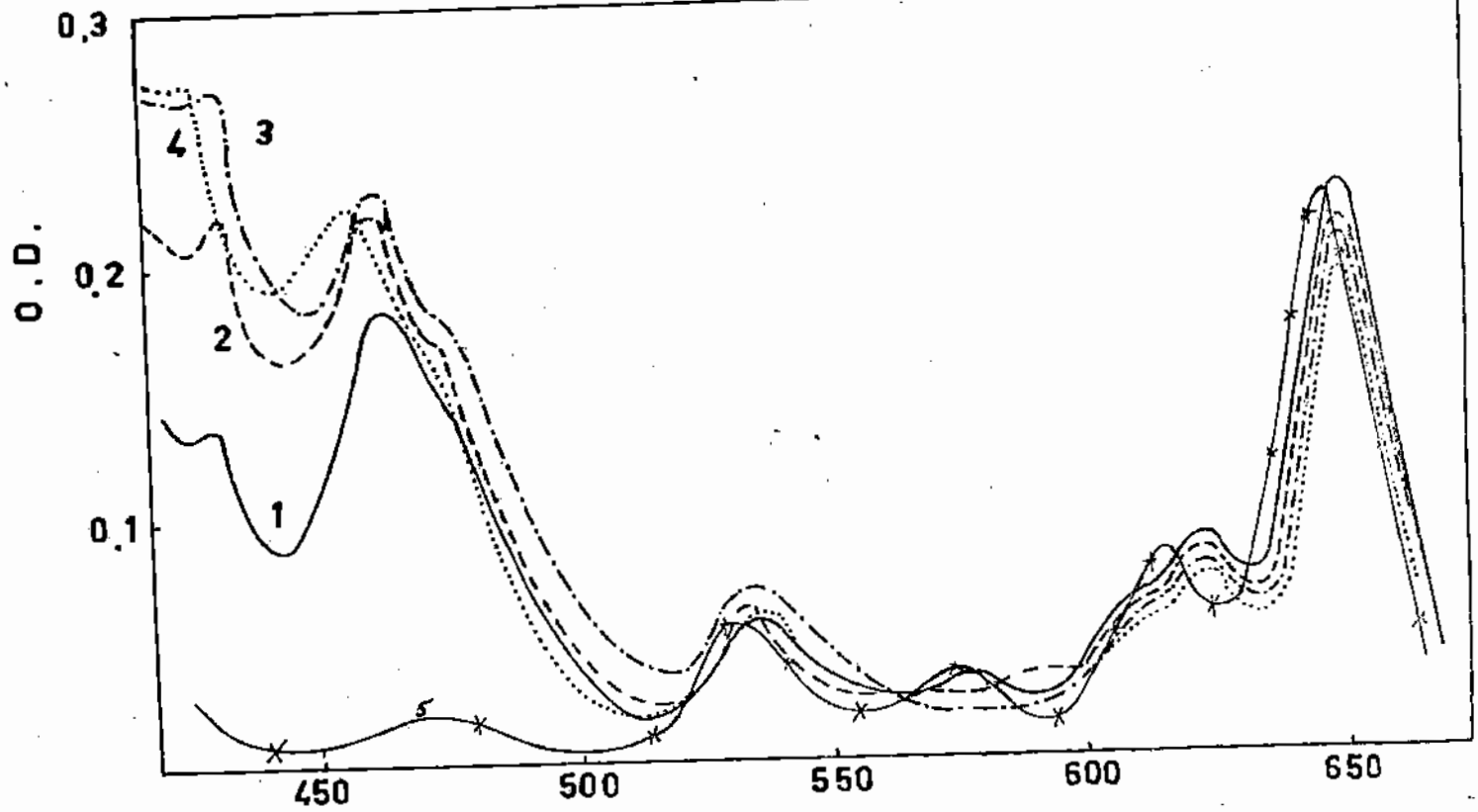
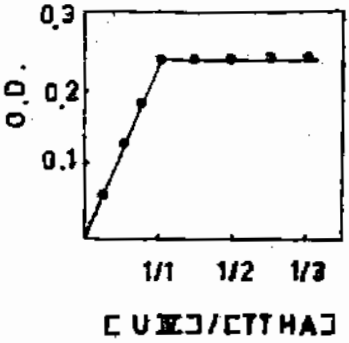
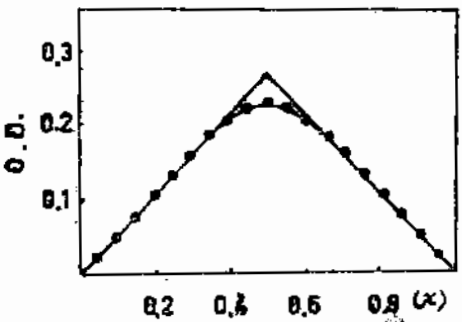


Fig. 1





$$x = \frac{[\ \text{U Ⅲ}\ ]}{[\ \text{U Ⅲ}\ ] + [\ \text{TTHA}\ ]}$$

Fig. 2 b

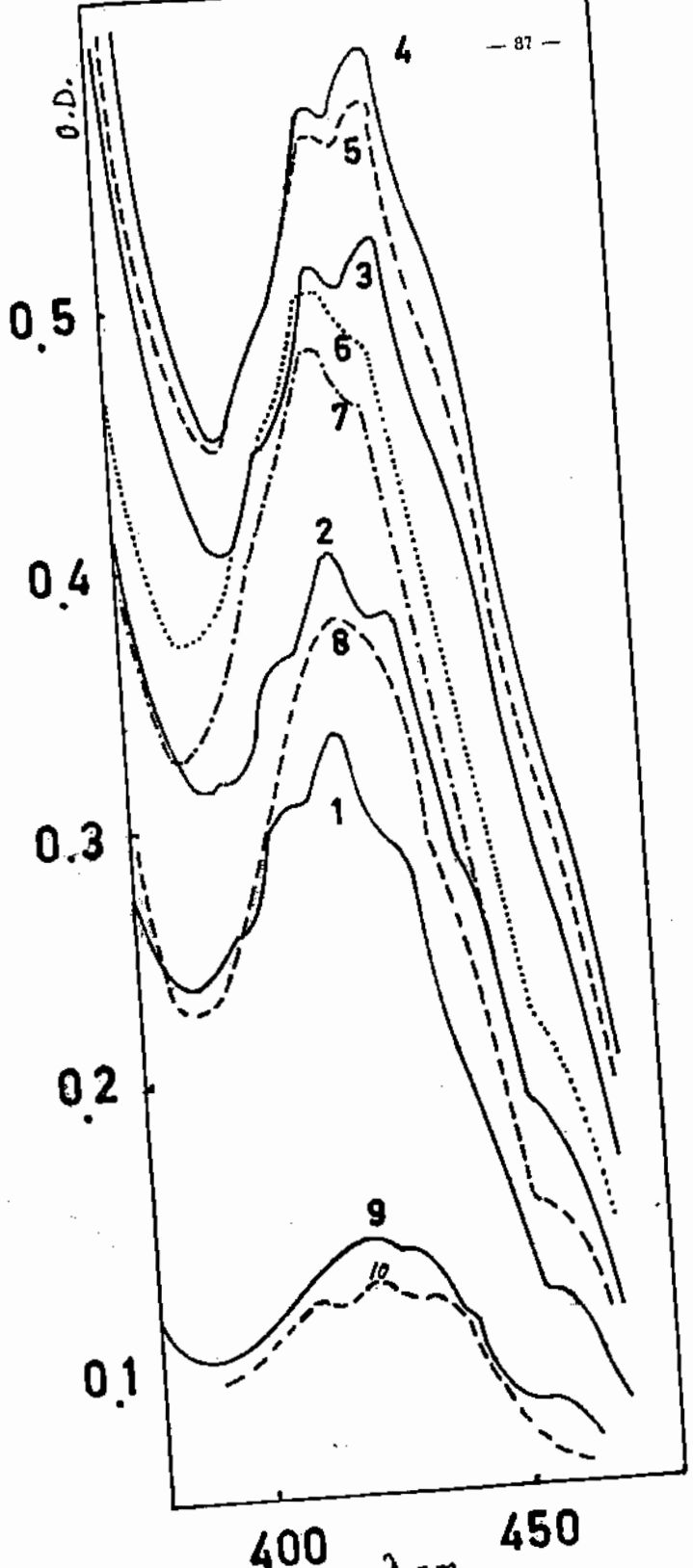
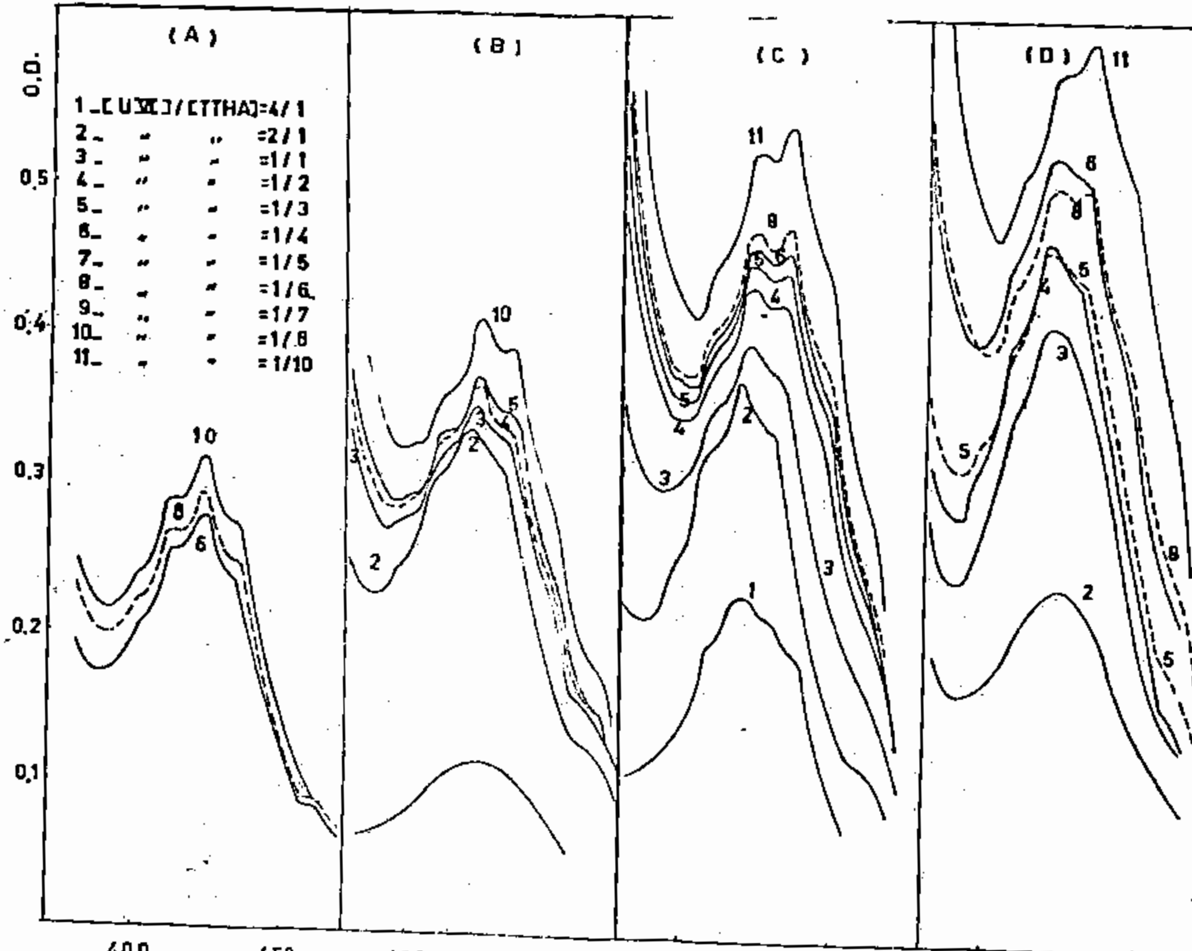


Fig. 3



(A)
(B)
(C)
(D)
O.D.
0.5
0.4
0.3
0.2
0.1
1_[UVI]/[TTHA]=4/1
2_ " " =2/1
3_ " " =1/1
4_ " " =1/2
5_ " " =1/3
6_ " " =1/4
7_ " " =1/5
8_ " " =1/6
9_ " " =1/7
10_ " " =1/8
11_ " " =1/10