

SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS A COMPLEXING AGENT

XII. DETERMINATION OF STABILITY CONSTANTS FOR THE COMPLEXES OF URANIUM AND TETRACYCLINE

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Stability constants for uranium-tetracycline complexes were determined by the method of average number of ligands, the method of limiting values, the method of two parameters and the method of weighted least squares. Solvent extraction technique was used to obtain experimental data.

Introduction

In previous work SAIKI et al.¹ used tetracycline (TC) to separate uranium from Th, Sc, Np, Ba, Pa, lanthanides and other ions, uranium being extracted into a solution of tetracycline in benzyl alcohol. CUNHA and NASTASI² used the same extracting solution of TC in benzyl alcohol to separate uranium from the fission products ¹⁴¹Ce, ¹⁴⁰La, ¹³⁷Cs, ⁹⁰Sr, ¹⁰³Ru, ¹⁴⁰Ba, ⁹⁹Mo, ^{99m}Tc, ¹³¹I and ¹³²Te. SAIKI and LIMA^{3,4} determined the stability constants for complexes of TC with thorium and all lanthanides except promethium.

The TC molecule presents three acidic groups, meaning tricarbonylmethane group, phenolic diketone and ammonium cation. The logarithm of the dissociation constants are respectively $pK_1 = 3.30$, $pK_2 = 7.68$, $pK_3 = 9.69$. LEESON et al.⁵ MAHGOUB et al.⁶ studied the infrared absorption spectrum of the uranyl - TC complex and suggested that, in the conditions of their experiments, the tricarbonylmethane group is involved in chelation with the UO_2^{2+} ion.

In this paper the techniques of solvent extraction, conductometric and potentiometric titrations were applied to study the formation of the $UO_2 - TC$ complexes. Formation constants were determined by solvent extraction techniques. Four methods of calculation^{3,4,7} were applied to get numerical values of the constants, viz. the two-parameter method, the limiting values method, the average number method and the weighted least squares method.

Experimental

All reagents used were of analytical grade. Deionized water was distilled in a quartz apparatus and used throughout. To avoid a variation of volumes in the organic and aqueous phases during extraction, benzyl alcohol and water were saturated with water and benzyl alcohol, respectively. TC solutions were prepared by dissolving TC hydrochloride (Laborterápica Bristol, SP) in water or benzyl alcohol. Aqueous solutions of TC were prepared every day and used within 6 hours after preparation since the ligand molecule decomposes in aqueous solution at room temperature.

Uranium solutions were prepared by dissolving U_3O_8 , previously calcined at $800^\circ C$, with drops of $HClO_4$ and HNO_3 and heating the mixtures to eliminate the excess of acids and next diluting with water to obtain a uranyl solution corresponding to 0.020M.

The extraction system was made up of 5.0 ml solution of TC in benzyl alcohol, sodium perchlorate at a concentration equal to 0.10M used as salting electrolyte to keep constant the ionic strength and 5.0 ml of an aqueous solution of uranium. Concentration of uranium varied from $1.0 \cdot 10^{-5} M$ to $2.0 \cdot 10^{-4} M$ and that of TC from $1.0 \cdot 10^{-3} M$ to $5.0 \cdot 10^{-3} M$. The pH of the aqueous phase was adjusted with dilute solutions of $HClO_4$ or $NaOH$.

The two phases were transferred to a separatory funnel and agitated for 30 minutes at $(25 \pm 1)^\circ C$. Previous experiments had shown that distribution equilibrium was attained in less than 10 minutes. After equilibrium the phases were separated by decantation followed by centrifugation in order to analyze uranium. From each phase 25 μl of solution was transferred to a filter paper with a surface of about 5 cm^2 and dried with infrared heat. Next uranium was determined by activation with epithermal neutrons.⁸ Counts of ^{239}U were carried out in a $NaI(Tl)$ detector on line with a 400 channel gamma-ray analyzer.

Concentration of free ligand in the aqueous phase $[A]$ was calculated in accordance with Reference 4, by the expression

$$pA = pK_1 - pH - \lg C_0 V_0 / (1 + D' V_0 V^{-1}) (1 + K_1 [H]^{-1}) V \quad (1)$$

where $pA = -\lg[A]$;
 K_1 — first dissociation constant of TC,
 C_0 — initial concentration of TC in the organic phase,
 V_0, V — volumes of organic and aqueous phases, respectively,
 D' — distribution ratio for the ligand TC.

Values of pA were calculated for solutions in which the pH was smaller than 5.5. Values of K_1 and D' were taken from Reference 4.

Results and discussion

Potentiometric titrations

The titration of the TC solution without uranium is presented in Fig. 1, Curve 1. In this curve there is an inflexion point around pH 5.5 that corresponds to neutralization of the hydrogen of the tricarbonylmethane group, $pK_1 = 3.30$. Determination of the second inflexion point, which would correspond to neutralization of the hydrogen of the phenolic diketone group, is rather uncertain since the difference between the values of pK_2 and pK_3 is smaller than four.

Potentiometric titration of the TC solution in which uranyl ion is present is shown in Fig. 1. Curve 2 shows that, for the same volume of NaOH added, there is a smaller increase of the pH value than when the titration is carried out without uranium. This indicates formation of complexes between uranyl ion and TC which occurs in solution with pH less than 5.5. For the range of pH from 7.0 to 9.0 there

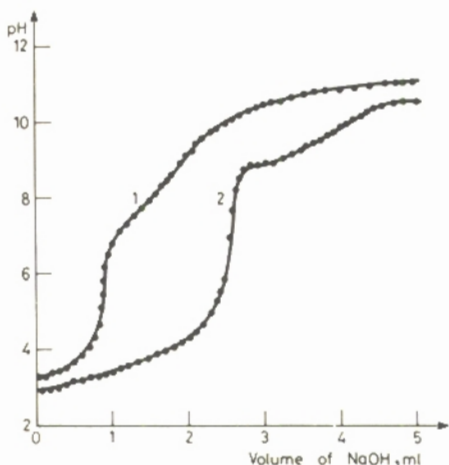


Fig. 1. Potentiometric titrations of 0.0010M TC with 0.116M NaOH. Curve 1 - no UO_2^{2+} ; curve 2 - UO_2^{2+} : TC = 1:1. Volume of TC solution: 100 ml

is formation of a precipitate and the titration gives erratic results. In solutions with pH less than 5.5 the dissociation of hydrogen of the phenolic diketone and ammonium cation groups is very small and can be neglected, TC being taken as a monoacid with a pK value equal to 3.30 ($H_3A \rightleftharpoons H^+ + H_2A$).

Conductometric titrations

The conductometric titrations were carried out in order to identify the chemical species formed between uranyl ion and TC. The titrating solution of TC was added in fractions of 0.2 ml. Specific conductance of the water used was equal to $1.4 \cdot 10^{-6}$ mho \cdot cm $^{-1}$. Values of the specific conductances were corrected by multiplying these values by $(V + v)/V$ in which V is the initial volume of the uranium solution and v the volume of the added titrating solution. Results of the titrations show the formation of complexes in which the $UO_2:TC$ ratios are equal to 1:1 and 1:2, Fig. 2.

Identification of the complexes by solvent extraction technique

In order to check if the complexes formed are mono or polynuclear the distribution ratio of uranium (D) was determined for three concentration values of uranium as a function of pH, the concentration of TC being kept constant. Results are presented in Fig. 3. A statistical F test and Student's t test⁹ applied to the set of values of Fig. 4 show that the corresponding straight lines are coincident at a confidence level of 0.95, i.e., the distribution ratios of uranium are independent

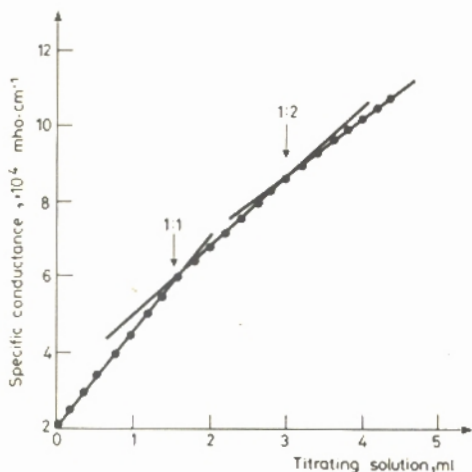


Fig. 2. Conductometric titration. Solution to be titrated: 3 ml of 0.20M $UO_2(NO_3)_2$ + 60 ml of water. Titrating solution: 0.040M TC

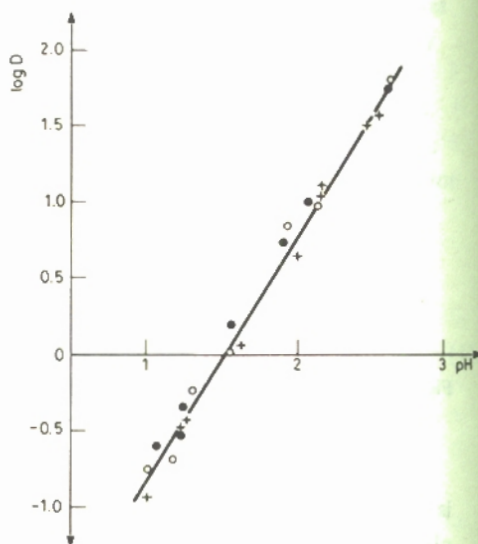


Fig. 3. Distribution ratio of uranium vs. pH. $[TC] = 0.0050M$; $[NaClO_4] = 0.10M$; $[U] = 1.0 \cdot 10^{-5} M$ (●), $8.0 \cdot 10^{-5} M$ (+), $2.0 \cdot 10^{-4} M$ (○)

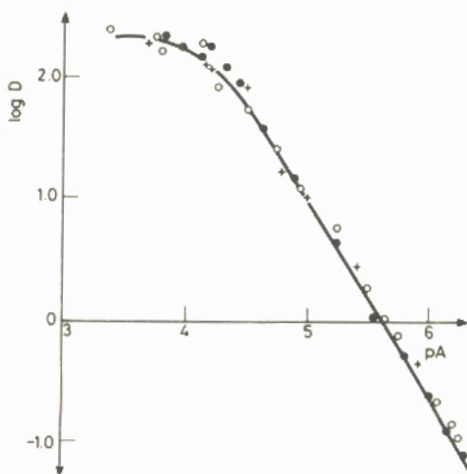


Fig. 4. Distribution ratio of uranium vs. pA for different concentrations of TC.
 [TC] = $5.0 \cdot 10^{-3}$ M (○); $2.5 \cdot 10^{-3}$ M (●); $1.0 \cdot 10^{-3}$ M (+)

of its concentration in the range $1.0 \cdot 10^{-5}$ M and $2.0 \cdot 10^{-4}$ M, indicating the formation of mononuclear complexes of uranyl ion and TC.^{7,10}

In order to check if the complexes are of the general formula MA_n , $MA_n(OH)_p$ or $MA_n(OH)_p(HA)_r$ the distribution ratio of uranium as a function of the logarithm of free ligand (pA) were determined for different initial concentrations of TC. Figure 4 shows that lg D is not dependent on the initial concentration of TC, being only a function of pA. This indicates formation of a complex of the type MA_n .^{7,10}

Calculation of the stability constants

The fundamental equation for the calculation of stability constants for the complexes MA_n from data obtained by the solvent extraction technique is⁷

$$D = I_0/I = K_D \beta_N [A]^N / \sum_{i=0}^N \beta_i [A]^i \quad (2)$$

where I_0, I — count rates for organic and aqueous phases, respectively,
 K_D — distribution constant of the complex MA_N ,
 β_n ($n=1,2$) — stability constants,
 $N=2$ — is the charge of uranyl ion.

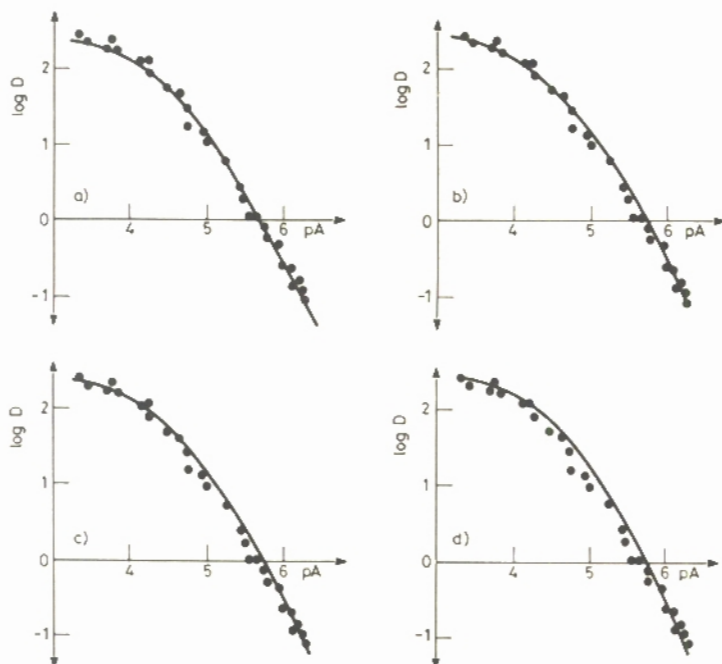


Fig. 5. Distribution ratio of uranium vs. pA. Dots represent experimental values. Curves are calculated values using constants obtained by the four methods: limiting value (a); two parameters (b); average number (c); least squares (d)

Table 1
Stability constants for uranyl – tetracycline complexes

Constants	Method			
	Average number	Limiting value	Two parameters	Least squares
$\lg \beta_1$	5.1	5.0	5.0	4.7 ± 0.1
$\lg \beta_2$	9.1	9.0	9.1	9.0 ± 0.1
K_D	—	286	—	274 ± 61

Ionic strength : 0.10M NaClO₄

Temperature : (25 ± 1) °C.

[UO₂²⁺] : 10⁻⁴ M to 10⁻⁵ M.

Initial concentration of TC in benzyl alcohol : 1.0 · 10⁻³ M to 5.0 · 10⁻³ M.

The experimental values of D and $[A]$ were used to obtain the values of K_D and β_n by the calculation methods already mentioned.

Table 1 presents the values of the formation constant for the complexes of uranyl ion and TC.

The calculated values of the stability constants were substituted into the fundamental Eq. (2) in order to see if such substitution would reproduce the experimental data. It is seen that the four methods of calculation give curves that correspond to the experimental points, Fig. 5. ●

MAHGOUB et al.⁶ had determined the stability constants for the 1:1 uranyl-tetracycline complex by spectrophotometry and they found the value $\lg \beta_1 = 5.08$, which is in agreement with the values presented in Table 1.

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