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THERMODYNAMICS OF URANYL COMPLEXES WITH THREONINE AND HYDROXYPROLINE

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ABSTRACT

The stability constants of uranyl complexes with threonine and hydroxyproline were studied in aqueous solution at 25 and 45°C by the Calvin–Bjerrum technique. Thermodynamic stability constants have been obtained by extrapolation of the values at various ionic strengths. The values of stepwise changes in ΔG, ΔH and ΔS have been reported.

INTRODUCTION

Threonine and hydroxyproline are biologically important substances as these are essential for growth. Extensive data are available on their complex formation with transition metal ions. As uranium(VI) forms a part of radioactive fallout and is found to form stable complexes, it can, therefore, affect the environment in which they interact. Complex formation between the uranyl ion and some different amino acids has already been reported by the authors[1,2]. No information is available on the complex formation of this ion with threonine and hydroxyproline. It was, therefore, desirable to carry out investigations on the stabilities of the uranyl ion complexes with these amino acids. The present paper deals with the determination of "practical" proton–ligand stability constants and thermodynamic metal–ligand stability constants by the Bjerrum–Calvin titration technique[3,4] as adopted by Irving and Rossotti[5] in aqueous solution.

The free energies of formation (ΔG), enthalpy (ΔH) and entropy changes (ΔS) involved in the formation of UO_2 complexes with threonine and hydroxyproline are also reported at an ionic strength of 0.05 M KCl at 25 and 45°C.

EXPERIMENTAL

Materials

Standard carbonate free potassium hydroxide[6] was used for potentiometric titrations. All inorganic salts were of Analar grade. $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ was used for preparing the solution. L-threonine and L-hydroxyproline were obtained from M/S E. Merck Lab., Germany. All the solutions were prepared in double glass distilled water.

Apparatus

A "systronic" pH meter with a glass and calomel electrode assembly was used to follow the change in pH during the titrations which were done at 25±0.1 and 45±0.1 °C in a constant temperature water bath.

Procedure

The following mixtures (total volume 20 ml) were titrated against standard alkali:

A. 2 ml of HCl (0.005 M)
B. A+2 ml of ligand (0.05 M), and
C. B+2 ml of metal ion (0.01 M).

An ionic strength of 0.1 M was maintained by the addition of calculated amount of potassium chloride. The plots of pH vs the volume of alkali required to reach the corresponding pH changes were plotted. The shapes of titration curves were as usual.

RESULTS

"Practical" proton–ligand stability constant

The calculations of the practical stability constants of proton complexes were done by plotting $\bar{n}_A$ versus pH and then applying various computational methods[7]. The values of the protonation constants of ligands at different ionic strengths and temperatures are summarized in Table 1.

TABLE 1

PROTON–LIGAND STABILITY CONSTANTS OF AMINO ACIDS AT 25 AND 45 °C

Values shown in parenthesis were made at 45 °C.

Amino acid	*Constants*	μ		
		0.05	*0.15*	*0.25*
Hydroxyproline	$\log K_1^H$	9.75 (9.45)	9.70 (9.40)	9.68 (9.37)
	$\log K_2^H$	1.85 (1.78)	1.84 (1.76)	1.83 (1.73)
Threonine	$\log K_1^H$	9.10 (8.75)	9.07 (8.70)	9.03 (8.60)
	$\log K_2^H$	2.20 (2.15)	2.17 (2.13)	2.15 (2.11)

Metal–ligand stability constant

For metal chelate formation taking place in steps in a homogeneous solution, the step formation constants are given by eqn (1)

$$K_n = C(\mathrm{ML}_n)/C(\mathrm{ML}_{n-1})\, C(\mathrm{L}) \qquad (n = 1, 2 \ldots N) \tag{1}$$

where K_n is called the metal–ligand stability constant. In the present case the formation constants have been obtained by analysis of the formation curves obtained by plotting

$\bar{n}$ against pL. The values of $\bar{n}$, the average number of ligands attached per metal ion, is calculated from eqn (2) of Irving and Rossotti[5]

$$\bar{n} = \frac{\{(V''' - V'')(N + E^{\circ})\}}{\{(V^{\circ} + V')\,\bar{n}_{A}\,T^{\circ}_{CM}\}}. \qquad (2)$$

The free ligand exponent pL has been calculated from eqn (3)

$$\mathrm{pL} = \log_{10}\left\{\frac{\left[\sum_{n=0}^{n=j} \beta^{H}_{n}(1/\mathrm{antilog}\,B)^{n}\,(V^{\circ} + V''')\right]}{\left[T^{\circ}_{CL} - \bar{n}T^{\circ}_{CM}\,V^{\circ}\right]}\right\} \qquad (3)$$

where β^{H}_{n} is the overall practical ligand stability constant. The formation curves (Fig. 1) were obtained by plotting $\bar{n}$ against pL and the method of least squares[7] was applied to evaluate the stepwise formation constants.

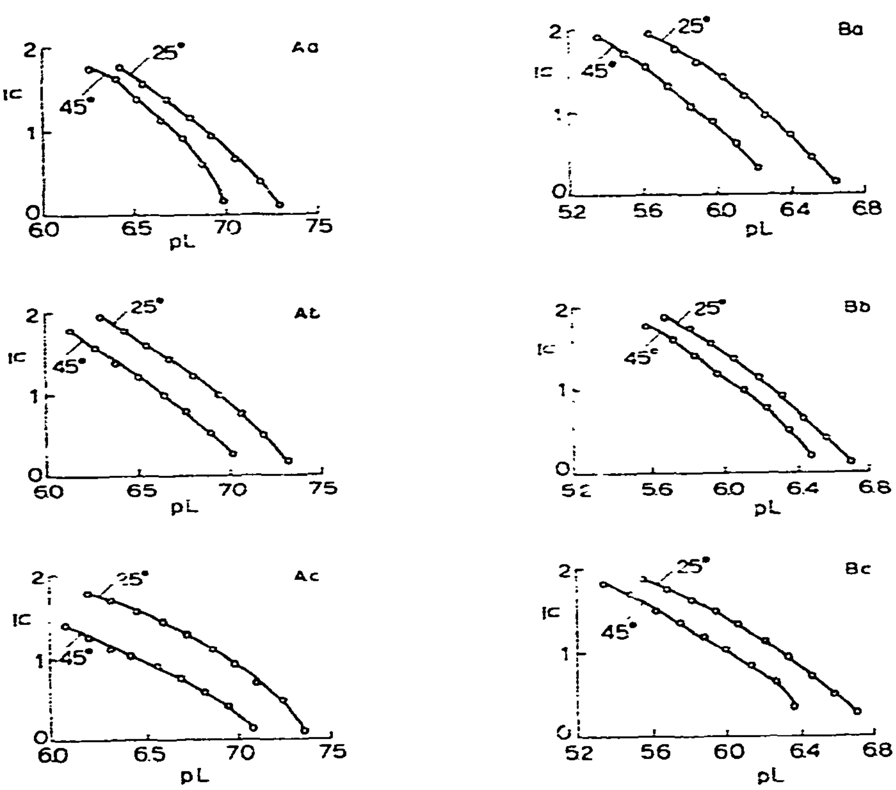

Fig. 1. Formation curves of uranyl–amino acids (A, hydroxyproline; B, threonine) at 25 and 45 °C, at three values of μ. a, $\mu = 0.25$; b, $\mu = 0.15$; c, $\mu = 0.05$.

For uranyl–amino acid complexes, the titration studies indicated that in the pH range 4.50–6.00 the complexes have 1:2 composition. The values of concentration stability constants at various ionic strengths and temperatures are given in Table 2.

The limits of errors for the stability constants are ±0.05 log units for log K_1 and log K_2.

TABLE 2

STABILITY CONSTANTS OF THREONINE–URANYL COMPLEXES AND HYDROXYPROLINE–URANYL COMPLEXES

T (°C)	*Constants*	*μ*		
		0.05	*0.15*	*0.25*
Threonine–uranyl complexes				
25	log K_1	6.35	6.30	6.22
25	log K_2	6.15	6.10	6.04
25	log β_2	12.50	12.40	12.26
45	log K_1	6.12	6.08	5.95
45	log K_2	5.92	5.82	5.70
45	log β_2	12.04	11.90	11.65
Hydroxyproline–uranyl complexes				
25	log K_1	7.02	7.00	6.96
25	log K_2	6.82	6.80	6.80
25	log β_2	13.84	13.80	13.76
45	log K_1	6.70	6.55	6.35
45	log K_2	6.50	6.40	6.20
45	log β_2	13.20	12.95	12.55

Thermodynamic stability constants

The thermodynamic formation constants have been obtained by extrapolation of the plots of log β_2 vs $u^{1/2}$ for metal–ligand systems to zero ionic strength[8]. The values are summarized in Table 3.

TABLE 3

THERMODYNAMIC STABILITY CONSTANTS OF URANYL COMPLEXES

Amino acid	*T* (°C)	*log β_2*
Threonine	25	12.68
	45	12.34
Hydroxyproline	25	13.90
	45	13.70

Thermodynamic parameters

The values of stepwise changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) at an ionic strength of 0.05 M are given in Tables 4–6. The stepwise changes in free energy and entropy were determined from eqns. (4) and (5)

$$\Delta G_j = -RT \ln \beta_j/\beta_{j-1} \tag{4}$$

and

$$\Delta G_j = \Delta H_j - T\Delta S_j \tag{5}$$

TABLE 4

FREE ENERGY DATA (in kcal mole^{-1}) OF URANYL–AMINO ACID COMPLEXES

Amino acid	T (°C)	$-\Delta G_1$	$-\Delta G_2$	$-\Delta G$
Threonine	25	8.66	8.39	17.05 (17.30)
	45	8.91	8.61	17.52 (17.96)
Hydroxyproline	25	9.58	9.30	18.88 (18.95)
	45	9.75	9.47	19.22 (19.94)

TABLE 5

ENTHALPY DATA (in kcal mole^{-1}) OF URANYL–AMINO ACID COMPLEXES

Amino acid	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H$
Threonine	4.99	4.99	9.98 (7.37)
Hydroxyproline	6.94	6.94	13.88 (4.34)

TABLE 6

ENTROPY DATA (in cal deg^{-1} mole^{-1}) OF URANYL–AMINO ACID COMPLEXES

Amino acid	T (°C)	ΔS_1	ΔS_2	ΔS
Threonine	25	12.31	11.41	23.72 (33.33)
	45	12.32	11.38	23.70 (33.30)
Hydroxyproline	25	8.86	7.92	16.78 (49.02)
	45	8.83	7.95	16.78 (49.05)

The enthalpy changes were determined by integration of the Van 't Hoff equation at two temperatures. The accuracy of ΔH values is ± 1.5 kcal mole^{-1} and that of ΔS values is ± 4 cal deg^{-1} mole^{-1}. In view of the difficulty of obtaining the thermodynamic stability constants, it may be noted that ΔG, ΔH, and ΔS values have been evaluated at an ionic strength of 0.05 M. For comparison purposes relative values would do, as under the same condition of ionic strength, the values of ΔG, ΔH and ΔS for these complexes will show the same variation as the values of the standard thermodynamic functions. However, the values of standard ΔG°, ΔH° and ΔS° which were obtained from extrapolated values of concentration stability constants to zero ionic strength, are given in parentheses in Tables 4–6.

DISCUSSION

It is evident from data (Table 2) that log K_1/K_2 values are positive for threonine and hydroxyproline complexes and greater stability is achieved at lower temperatures.

It is also evident that the stability decreases with the increase in ionic strength. It is indicated in Tables 5 and 6 that the values of ΔH are negative and those of ΔS are positive for uranyl complexes with both the ligands. This shows that both the terms are favourable for the formation of complexes. It may be further noted that hydroxyproline complexes are slightly more stable than their corresponding threonine complexes.

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