Electrometric Study on Uranyl(II) and Vanadyl(II) Complexes of DL-Tryptophan

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COMPLEX formation of Uranyl (UO_2^{+2}) and Vanadyl (VO^{+2}) with DL-Tryptophan have been studied employing potentiometric techniques. Both form 1 : 1 and 1 : 2 complexes, in the pH range 3.00-6.50 whose log β_{stab} values have been determined by Calvin-Melchior's extension of Bjerrum's method. The overall stabilities (log β) of uranyl and vanadyl are 14.37, 14.80 at 20°C ; 13.52, 15.46 at 30°C and 13.37, 15.75 at 40°C respectively. The overall changes in thermodynamic functions ΔG, ΔH and ΔS accompanying the complexation reactions have been determined at 30°C.

AMINO-acid, containing active $-NH_2$ and $-COOH$ groups have a wide variety of applications in medicine, biology and other chemical fields. Several metal ions have the ability of complex formation with amino acids which are involved in several metabolic and enzymatic activities of human beings and have a key role in nitrogen assimilation. Saxena and coworkers[2-4] have studied several such metal complexes of amino acids which have found useful applications in biological and pharmaceutical fields. The present communication describes the chemistry of UO_2 (II) and VO (II) complexes with DL-Tryptophan ; their composition, stability constant and thermodynamic functions, and accompanying the complexation reactions at different temperatures. There is however no reference in the literature on these investigations and hence this work has been taken.

EXPERIMENTAL

DL-Tryptophan referred herein as (HA) was obtained from B.D.H. Poole England and all other chemicals were of AnalaR-grade. Fresh solutions of metal ions $UO_2(NO_3)_2.6H_2O$ and $VOSO_4.H_2O$ were prepared in a calculated quantity of $HClO_4$ to check hydrolysis.

The entire study was carried out in an inert atmosphere of nitrogen and fresh solutions were used to avoid effects of ageing and oxidation.

pH measurements were made on a Toshniwal digital pH meter with glass-calomel electrode assembly in a nitrogen atmosphere. The temperature of the cell was maintained by thermostat (U_1-type, German) having an accuracy of ± 0.1°C. Requisite quantities of $NaClO_4$ were added to the solution mixtures for maintaining the constant ionic strength ($\mu = 0.1$M). The final volume, in all the mixtures was maintained upto 25 ml with doubly distilled water. For determining stability constants at 20°C, 30°C and 40°C the ratio of metal to ligand was always one to four (1 ; 4) and (10.0 mM) $HClO_4$ is used for initial lowering of buffer region. For quantitative detection for complex formation stoichiometric titrations were performed between solutions containing HA and the metal ion in different molar ratios against (0.1M) NaOH. The experimental procedure described earlier involved a series of pH metric titrations of HA in presence and absence of metal ion against standard (0.1M) NaOH.

RESULT AND DISCUSSION

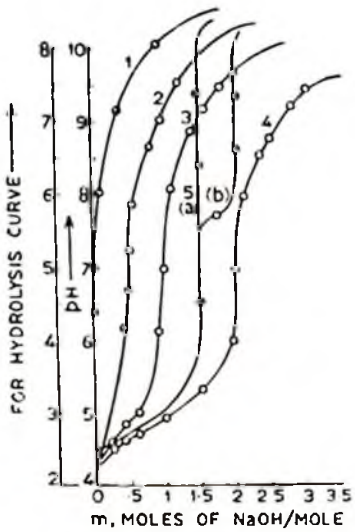
Stoichiometry : The composition of the complexes formed during the interaction of $UO_2(NO_3)_2.6H_2O$ and $VOSO_4.H_2O$ with DL-Tryptophan was established by measuring the magnitude of proton displacement during the titration of ligand in the absence and presence of metal ion at different ratios. Titration curve (Fig. 1, curve 1) corresponds to the neutralisation of acid group of the ligand. The addition of an equimolar concentration of metal ion greatly alters the shape of free ligand titration curve (Fig. 1, curve 4) indicating the complex formation which results in the lowering of buffer region due to proton displacement.

$$M^{+n} + HA \rightleftharpoons MA^{+(n-1)} + H^{+} \qquad (1)$$

where M^{+n} stands for UO_2^{+2} and VO^{+2}.

Since the extent of proton displacement depends on the relative affinity of the ligand for hydrogen ion and metal ion, it is obvious from the curves (Fig. 1, curves 2, 3, 4) that the affinity of M^{+2} ions is not great enough to compete with the relatively high concentration of hydrogen ions.

The inflection at m = 2 (m, being the mole of NaOH per mole of HA) suggests the formation of MA_2 as



(1) 4·0 mM HA (2) 4·0mM HA + 1·0mM $UO_2(NO_3)_2$
(3) 4·0 mM HA + 2·0mM $UO_2(NO_3)_2$
(4) 4·0mM HA + 4·0mM $UO_2(NO_3)_2$
(5) HYDROLYSIS CURVE
(a) 4·0 mM $HClO_4$
(b) 4·0 mM $HClO_4$ + 1·00 mM $UO_2(NO_3)_2$

FIG. 1 POTENTIOMETRIC TITRATIONS OF DL-TRYPTOPHAN IN ABSENCE & PRESENCE OF UO_2^{++} WITH 0·1 NaOH

the highest complex along with $M(OH)_2$ at higher pH values 7.5 in accordance with the following equation.

$$MA^+ + OH^- \rightleftharpoons \tfrac{1}{2} MA_2 + \tfrac{1}{2} M(OH)_2 \qquad (2)$$

The hydrolysis of the title metal salt was studied. Fig. 1, curve 5 shows the hydrolysis curve of uranyl salt which is taken as a representative case (hydrolysis curve of other metal salts has not been given for the sake of brevity).

From these curves, it is observed that no hydroxo complexes are formed upto pH range 5.80 and 5.73 for UO_2^{+2} and VO^{+2} salts respectively.

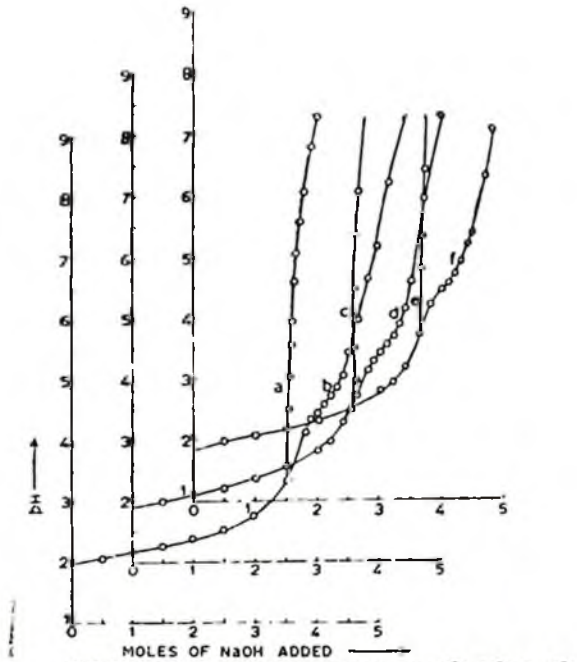
When metal ion and ligand are mixed in the ratios 1 : 4, 1 : 2 and 1 : 1, the inflections are obtained at m = 0.5, = 1.0 and = 2.0 respectively (Fig. 1 curves 2, 3, 4). These inflections suggest the formation of MA^+ and MA_2 corresponding to 1 : 1 and 1 : 2 complexes respectively with considerable overlapping according to the following equations :

$$M^{+2} + HA + OH^- \rightleftharpoons MA^+ + HOH \qquad (3)$$

$$MA^+ + HA + OH^- \rightleftharpoons MA_2 + HOH \qquad (4)$$

$$M^{+2} + 2HA + 2OH \rightleftharpoons MA_2 + 2HOH \qquad (5)$$

i. e. 1 : 1 and 1 : 2 complexes are being formed simultaneously and in all the above cases metal complexes may disproportionate at higher pH (= 7.5) values to give normal metal hydroxide which precipitate along with the simultaneous formation of the higher complexes.



CURVE a, c & e: 8·0mMHA + 10 mM $HClO_4$ AT 20°C, 30°C & 40°C RESPECTIVELY
CURVE b, d & f. 8·0mM HA + 2·0mM UO_2^{++} + 10·0mM $HClO_4$ AT 20°C, 30°C & 40°C RESPECTIVELY

FIG 2 POTENTIOMETRIC TITRATION OF DL-TRYPTOPHAN IN ABSENCE & PRESENCE OF UO_2^{++} WITH 0·1 M NaOH AT μ=0·10M $NaClO_4$

Formation of complex species between UO_2^{+2} and VO^{+2} with DL-Tryptophan may be explained as a five membered ring (Fig. 4).

STABILITY CONSTANTS

Calvin and Melchior's extension of Bjerrum's method has been employed for the determination of stability constants of complexes. The pH titrations of HA solution at ionic strength $\mu = 0.1M$ ($NaClO_4$) and $HClO_4$ concentration (10.0mM), for initial lowering of buffer region in absence and presence of metal ion were carried out at 20°C, 30°C and 40°C against 0.1M NaOH and the concentration of the bound ligand, calculated from the horizontal distance between the corresponding curves was divided by the total metal ion concentration, to obtain the formation function ($\bar{n}$). At any pH, the value of free lingand concentration [A] was calculated from the relation :

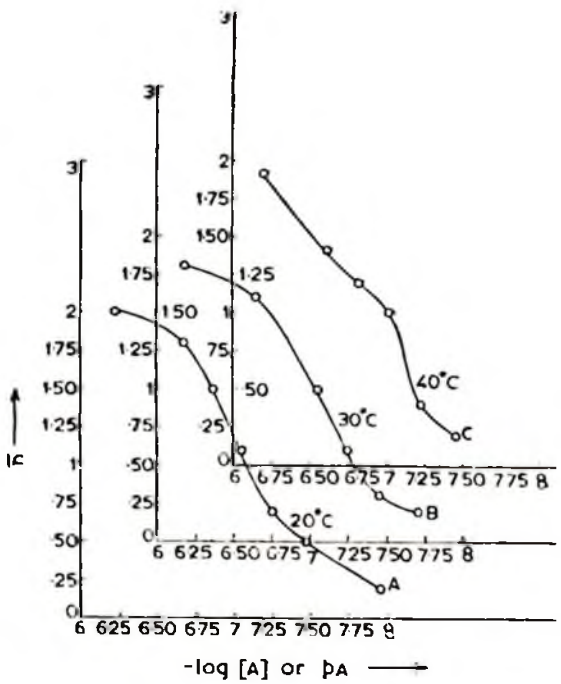


FIG. 3 FORMATION CURVES AT 20°C, 30°C & 40°C FOR UO_2^{+2} COMPLEXES OF HA

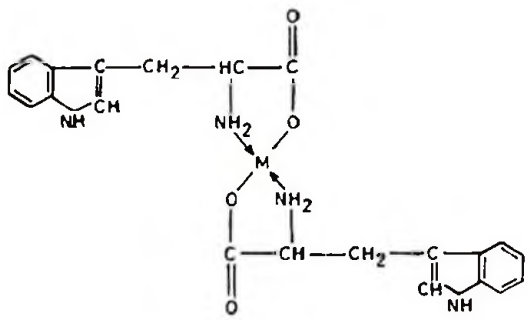


FIG. 4 COMPLEX SPECIES OF UO_2^{+2} AND VO^{+2} WITH DL-TRYPTOPHAN.

$$[A] = \frac{[\text{Ligand}]_{\text{Total}} - [\text{Ligand}]_{\text{Bound}}}{[(H^+)/Ka] + 1}$$

where k_a is the dissociation contant of HA 4.677×10^{-10} for tryplophane. The formation curves obtained at different temperatures by ploting $\bar{n}$ *Vs.* pA reveal the formation of 1 : 1 and 1 : 2 complexes for UO_2^{+2} has been given for sake of brevity. The values of stability constants for uranyl and vanadyl complexes with DL-Tryptophan at 20°C, 30°C and 40°C are given in Table I.

TABLE I

Stepwise metal ligand stability constant of UO_2 (II) and VO (II) complexes of DL-Tryptophan at different temperatures (μ = 0.1M $NaClO_4$)

Complexes	Values of stability constant as at * 20°C	30°C	40°C
Uranyl (II)			
log K_1	7.48	7.30	7.18
log K_2	6.88	6.23	6.20
Vanadyl (II)			
log K_1	7.58	8.01	8.08
log K_2	7.23	7.45	7.68

* Uncertainty limit = ±0.04 units
log β = log K_1 + log K_2

THERMODYNAMIC FUNCTIONS

The overall changes in thermodynamic functions, free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complexation reaction have been determined at 30°C with the help of following equations and given in Table II.

$\Delta G = -RT \ln\beta$ ($\beta = K_1K_2$, overall stability constant), ΔH is determined with the help of an isobar $(d \ln \beta)/dT = \Delta H/RT^2$, ΔS is then evaluated from the relation.

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

TABLE II

Thermadynamic Functions

Metal complexes	ΔG (Kcal/mole)	ΔH (Kcal/mole)	ΔS (cal/mole/deg)
Uranyl (II)	−18.75	−34.13	−50.74
Vanadyl (II)	−21.43	26.61	158.54

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