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POTENTIOMETRIC STUDIES ON THE COMPLEX FORMATION BETWEEN HEXAVALENT URANIUM AND TROPOLONES

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ABSTRACT

Thermodynamics of the complexation of uranium(VI) with tropolone (HTP) as well as β-isopropyltropolone (HIPT) have been studied in 50 vol.% water–dioxane medium at 25 and 35 ± 0.01°C adopting the Bjerrum–Calvin pH-titration technique as applied by Van Uitert and Haas. Both the ligands are weak monoprotic acids. Uranium(VI) forms 1:1 and 1:2 chelates with both ligands; the order of stability being $\log K_1 > \log K_2$. The stability invariably increases with an increase in temperature in both aqueous and water–dioxane media. The changes in ΔG^0, ΔH^0 and ΔS^0 at 25 and 35°C for the first stepwise formation constants have also been computed. Uranyl tropolonates are entropy stabilized, the enthalpy change values being positive. Factors affecting chelate stability are briefly discussed.

INTRODUCTION

Tropolone (2-hydroxy-2,4,6-cyclohepta-trienone) and its ring-substituted derivatives possess potential chelating structures through their electronegative atoms. Chelate complexes of tropolone (**I**) (HTP) and (β-isopropyltropolone (**II**) (HIPT) with transition metals, and particularly actinides, are substantially stable both in neutral and acidic solutions [1–9].

(**I**) R = H, tropolone (HTP)
(**II**) R = $-CH(CH_3)_2$, β-isopropyltropolone (HIPT)

This is generally attributed to the extra stability conferred by the delocalized π-system of the pseudo-aromatic ring of the ligand anions on the five-membered chelate ring formed by the α-diketone group and the central coordinating metal ion. Extensive studies with various tropolonates by Muetterties

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et al. [10–12] have clearly established that the low resultant charge, compact planar conformation, and relatively small "bite" of the bidentate tropolonato ligand are conducive to attaining high coordination numbers (7–10) by the larger triply and quadruply charged cations.

Numerous analytical applications of HTP and HIPT have already been reviewed [5,1,3,14]. Relatively little data exist concerning composition, structure and stability of uranyl complexes of both these ligands in solution. Most of the effort has, however, been restricted to the evaluation of their stoichiometric metal–ligand stability constants valid for some specific set of conditions [8,15]. To date, no value relative to the thermodynamic formation constant of uranyl tropolonate seems to have been reported [3,5]. The usefulness of data on metal–ligand stability constants in analytical chemistry arises from their important application in predicting values of solution parameters appropriate for analytical estimations. Also, a detailed knowledge of such equilibrium constants and related standard thermodynamic parameters is essential both in suggesting improvements in techniques of separation and in helping to understand the bonding and stereochemistry of complex species.

The present paper systematically investigates the interaction of HTP and HIPT with uranyl ions in a 50 vol.% dioxane–water mixture at 25 and $35 \pm 0.01^\circ$C adopting the Bjerrum–Calvin pH-titration technique as modified by Van Uitert and Haas [16]. It provides information concerning stoichiometry, stability and associated standard thermodynamic functions. The isopropyl derivative (**II**) was chosen because it can be compared with the widely used parent compound, HTP (**I**), so that the influence of the acyl substituent on M : L formation constants could be gauged. Aqueous dioxane is employed as the solvent medium because of the inadequate solubility of the reagents and their metal chelates in water.

EXPERIMENTAL

All the chemicals used were of AR (BDH) or GR (Merck) grade. Dioxane was purified by the recommended procedure [17]. Both HTP and HIPT, procured from Koch Light, U.K., were used as supplied. Uranyl perchlorate was prepared by the action of concentrated $HClO_4$ with orange uranium trioxide. After crystallization from aqueous acidic solution, the salt was dissolved in 0.01 M $HClO_4$ and the UO_2^{2+} content determined volumetrically using a Jones Reductor and cerimetric titration. An aqueous solution (10%) of tetramethyl ammonium hydroxide (TMAH) titrant was standardized against potassium hydrogen phthalate and diluted to 0.1 M; the proportion of dioxane and water was also 1 : 1.

All pH measurements were made with an Orion Research pH meter, model 701A, which can be read to 0.001 pH units.

Titration procedure

A weighed quantity of reagent, corresponding to a 0.01 M solution in a final volume of 50 ml, was placed in a dry titration vessel to which was added 25 ml of freshly distilled dioxane. Metal salt solution (5 ml, ~ 0.005 M) and $HClO_4$ (10 ml, 0.01 M) were then added to yield a 50 vol.% final composition of dioxane–water in the mixture. Due allowance for contraction in volume on the mixing of two solvents was made [18,19].

The titration vessel with its contents was then thermostated at 25 or 35 ± 0.01°C. The glass and calomel electrodes were placed in the titre and titrated by adding small aliquots of TMAH and noting the pH meter reading. Titrations were repeated until two sets of values differing by only ± 0.01 pH unit were obtained. A 10 : 1 ratio of the ligand to metal ion concentration was invariably maintained in order to satisfy the highest possible coordination number of the metal ion under investigation. For determining the thermodynamic acid dissociation constant of HTP and HIPT, T_{pK_a}, essentially the same procedure was followed without the addition of metal ion solution [20,21].

CALCULATIONS

Values of stepwise formation constants, K_1 and K_2, for the systems UO_2^{2+}–ligands were evaluated by least-squares analysis (rejecting the most divergent data, especially for low values of the $\bar{n}$ function) as given by Albert and Serjeant [22]. Procedural details of the calculations have been published elsewhere [23]. Other computational methods, viz. interpolation at half $\bar{n}$ values (Bjerrum's half integral method) as well as pointwise calculation [24], employing the following general equation, were also utilized for $\log K_n$ calculations.

$$\log K_n = \mathrm{pL} + \log[\bar{n} - (n-1)/(n-\bar{n})]$$

However, the constants are best evaluated by the least-squares method, which makes use of all the experimental data incidental to the plot of $\bar{n}/(\bar{n}-1)[L^-]$ against $(2-\bar{n})[L^-]/(\bar{n}-1)$ to obtain the intercept, K_1, given by the equation

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})[L]}{(\bar{n}-1)} K_1K_2 - K_1$$

Details regarding the calculations of standard thermodynamic functions (ΔG^0, ΔH^0, ΔS^0) and other relevent information have already been published [25].

RESULTS AND DISCUSSION

From a perusal of the metal–ligand formation curves obtained by plotting pL vs. $\bar{n}$ data for UO^{2+}–TP (Fig. 1) and UO^{2+}–IPT (Fig. 2) systems, it is evident that the curves are continuous and do not flatten at integral values of $\bar{n}$. Maximum $\bar{n}$ values obtained for UO^{2+}–TP and UO^{2+}–IPT systems are 1.2 and 1.5, respectively, which is in fine accord with the earlier results reported for UO^{2+}–TP [5]. The $\bar{n}$ calculations could not, however, be continued due to precipitation. In both cases, plots of $\bar{n}/(1-\bar{n})[L^-]$ vs. $(2-\bar{n})[L^-]/(1-\bar{n})$ are straight lines with a distinct slope instead of being parallel to the abscissa, indicating the formation of both 1 : 1 and 1 : 2 metal–ligand complexes. Values of thermodynamic stepwise formation constants, $T_{\log K_1}$ and $T_{\log K_2}$ evaluated by the various methods are in good agreement (Table 1) and follow the sequence $\log K_1 > \log K_2$. Compared to the graphical method, these computational methods provide greater statistical accuracy and yield true thermodynamic constants at all points. Although the values obtained by the least-squares method would be more acceptable, it may be seen that interpolation at half integral values is also quite representative of the stability constants. The $T_{\log K_n}$ values are positive and increase on increasing temperature. This shows that higher temperatures favour the formation of complexes. Results of the T_{pK_a} determination of HTP and HIPT have been published elsewhere [20,21]. Since activity coefficient corrections have been applied, the $T_{\log K_n}$ values reported here are

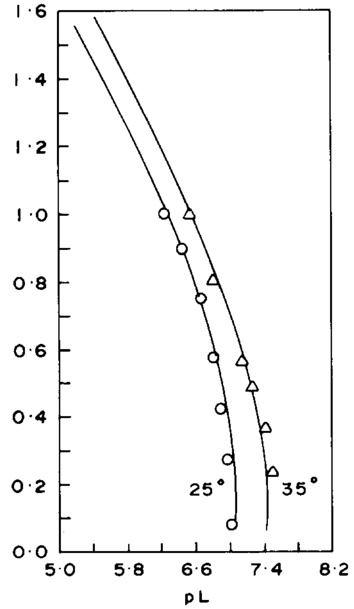

Fig. 1. Formation curves of uranyl complexes of tropolone.

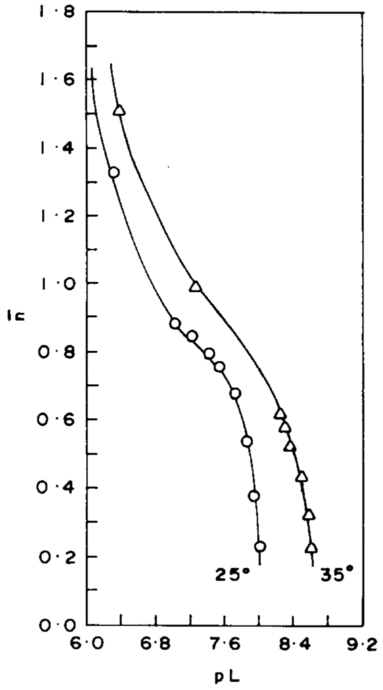

Fig. 2. Formation curves of uranyl complexes of β-isopropyl tropolone.

thermodynamic constants which are reproducible to ±0.05 log units in triplicate determinations. Variations in the initial concentrations of UO_2^{2+} and reagents yielded results varying by ±0.10 log units. There was no evidence of metal ion hydrolysis, polynuclear species or protonated complexes.

As normally encountered, the average stability constants, $T_{\log K_{Av}}$, are consistently lower than T_{pK_a} of both ligands. Separation factors, $T_{\log(K_1/K_2)}$, are always found to be positive. For tropolone these are well within the expected range which implies little or no steric hindrance to the addition of a second chelate group and further suggests that the formation of 1 : 1 and 1 : 2 complexes occurs with equal ease. Contrary to this, relatively higher values of $T_{\log(K_1/K_2)}$ in the UO_2^{2+}–IPT system evidently suggest the presence of an unusual opposition to the formation of a 1 : 2 chelate. Such a large ($\log K_1 - \log K_2$) difference has also been reported for uranyl isotropolonate in water–ethanol media [15]. In the case of chelating agents having bulky substituents near the donor atoms, such steric hindrance causes separation factors to be abnormally high. This has been demonstrated for *N*-substituted ethylenediamine complexes of Ni^{2+} [26].

The formation constants thus evaluated for M : L complexes in aqueous dioxane medium permit us to approximate the stability of the uranyl chelate

TABLE 1

Thermodynamic stepwise formation constants of UO_2^{2+}–TP and UO_2^{2+}–IPT systems [a]

Constant	Method of computation [b]	In 50 vol.% water–dioxane				In water			
		25°C		35°C		25°C		35°C	
		HTP	HIPT	HTP	HIPT	HTP	HIPT	HTP	HIPT
T_{pK_a}	L	8.53	8.97	8.76	9.19	6.90	7.29	7.05	7.48
$T_{\log K_1}$	L	7.01	8.56	7.77	8.92	5.38	6.88	6.06	7.21
	B	7.33	8.47	7.73	8.97	5.70	6.79	6.02	7.26
	P	7.29	8.55	7.75	9.01	5.66	6.87	6.04	7.30
$T_{\log K_2}$	B	5.52	6.33	5.83	6.60	3.89	4.65	4.12	4.89
	P	5.53	6.18	5.83	6.49	3.90	4.50	4.12	4.78
$T_{\log K_{av}}$ [c]	P	6.41	7.36	6.79	7.75	4.78	5.68	5.08	6.04
$T_{\log(K_1/K_2)}$ [c]	P	1.76	2.37	1.92	2.52	1.76	2.37	1.92	2.52

[a] $[UO_2^{2+}] = 0.00066$ M; [ligand] = 0.01 M; $[N(CH_3)_4OH] = 0.1$ M.

[b] L: values obtained by the least-squares method; maximum scatter in log K_1 is ±0.05. B: Values calculated from Bjerrum's half integral method. P: Values calculated by pointwise computation. The values of $T_{\log K_1}$ are the average of at least ten titration points.

[c] Values of $T_{\log K_{av}}$ and $T_{\log(K_1/K_2)}$ have been computed from formation constants obtained by pointwise calculations.

in water under the same conditions, following the relationship

$$\log K_1 - \log K_1(\mathrm{W}) = \mathrm{p}K_\mathrm{a} - \mathrm{p}K_\mathrm{a}(\mathrm{W})$$

proposed by Irving and Rossotti [27] for ML type complexes. Here the symbol (W) represents the corresponding values of K_1 and K_a in water.

Although the above relationship is valid for 1 : 1 complexes, approximations for 1/2 log β_2(W) were also tried using the experimentally obtained log β_2 value. Values of log K_1(W) and log K_2(W) thus calculated are also given in Table 1. The validity of the above relationship has been tested in a recent publication [28] wherein it has been observed that a good approximation on the basis of the above equation could be achieved only for K_1 but was not as accurate for K_2. Therefore, the extrapolated K_2(W) values given in Table 1 are somewhat uncertain.

Stepwise formation constant data summarised in Table 1 reveal that isopropyl tropolonate complexes are comparatively more stable than the corresponding tropolonate complexes in aqueous as well as mixed water–dioxane media at both temperatures. To a first approximation, this may be attributed to the more basic nature of HIPT, i.e., its higher $T_{\mathrm{p}K_\mathrm{a}}$ than that of HTP, and also to the electron-donating effect of the isopropyl group which tends to strengthen the M–L bond by increasing the negative charge on the oxygen of the O–M bond.

Thermodynamic functions

Thermodynamic functions, viz. ΔG^0, ΔH^0 and ΔS^0, associated with UO_2^{2+}–TP and UO_2^{2+}–IPT chelation reactions are recorded in Table 2. In view of the large uncertainties present in the evaluation of $T_{\log K_2}$, parameters corresponding to the formation of 1 : 2 complexes have not been included. The uranyl tropolonates are formed spontaneously as evidenced by the negative free energy of formation values (ΔG^0). The positive ligational enthalpy change values (ΔH^0) ensure that the metal–ligand complexation reactions are endothermic. The relatively small ΔH^0 values compared with

TABLE 2

Thermodynamic functions of uranyl tropolonates in 50 vol.% water–dioxane

System	Formation constant [a]	ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal deg^{-1} mol^{-1})	
		25°C	35°C		25°C	35°C
UO_2^{2+}-TP	log K_1	−9.56	−10.95	31.97	139.36	139.36
UO_2^{2+}-IPT	log K_1	−11.68	−12.58	15.14	89.9	90.3

[a] Thermodynamic functions computed from formation constants obtained by least-squares analysis. The error in ΔG^0 or ΔH^0 lies in the range 0.2–0.5 kcal mol^{-1} and that for ΔS^0 is 0.5 cal deg^{-1} mol^{-1}.

large values of ΔS^0 indicate entropy as the principal driving force for formation of metal complexes in aqueous dioxane media. An increase in randomness in the system will increase the stability of the complex, entropy being a solvent property.

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