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Thermodynamic Study of Formation of the Complexes of Thorium(IV) with Xylenol Orange at Different Temperatures

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The stability constants of the complexes of thorium(IV) ion with xylenol orange were determined in aqueous solution at 15, 20, 25, 30, 35 ºC and also 0.1 mol dm^{-3} ionic medium using a combination of potentiometric and spectrophotometric techniques. Sodium perchlorate was used to maintain the ionic strength. The composition of the formed complexes was determined and shown that thorium(IV) forms two mononuclear 1:1 species with the ligands, of the type Th(XO) and $ThH_2(XO)_2$ in the pH range of 2-6. The logarithms of the cumulative stability constants, β_{xyz}, of the complexes, $[(\text{Metal ion})_x (H^+)_y(\text{ligand})_z]$, are log β_{111} and log β_{122} : 8.58, 8.13, 7.89, 7.64, 7.42 and 17.09, 16.84, 16.64, 16.49, 16.33 at 15, 20, 25, 30 and 35 ºC, respectively. Some thermodynamic parameters were also calculated at different temperatures. ΔG, ΔH and ΔS values were obtained -19.636 KJ mol^{-1}, -42.622 KJ mol^{-1} and -77.095 J mol^{-1} k^{-1} for ThH(XO) and -41.330 KJ mol^{-1}, -27.768 KJ mol^{-1} and 45.486 J mol^{-1} k^{-1} for $ThH_2(XO)_2$ at temperatures were related, respectively.

Key Words: Complexation, Stability constant, Dissociation constant, Potentiometry, Spectrophotometry.

INTRODUCTION

Thorium is the most abundant radioactive element in nature[1,2]. It can capture slow neutrons and form ^{233}Th, which converts into the fissionable ^{233}U through two β-decays; thus thorium has been used as nuclear fuel[1,2]. Because of its relatively low radioactivity, Th(IV) is also a surrogate for Pu(IV) in nuclear waste separation studies. At pH 7.4 (physiological pH) thorium salts hydrolyzes to form colloidal particles of $Th(OH)_4$. Thorium is a toxic heavy metal and hence either Th(IV) ion or its hydroxide colloids readily react with *in vivo* proteins, amino acids and nucleic acids to form stable complexes which are deposited in the body[3,4], primarily in the liver,

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bone and bone marrow, spleen and kidneys[4,5]. For some time a goal of this laboratory has been the development of specific sequestering agents for the actinides.

Thorium(IV) chemistry presents an excellent area of research, because of its possibility of formation of compounds with high coordination number, a feature sparingly observed in transition metal chemistry. The coordination chemistry of Thorium(IV) has been less extensively investigated[6,7]. Th(IV) with an ionic radius 0.99 Å and a charge of +4 fulfils the optimum condition required for a high coordination. In view of the variation in stoichiometry from ligand to ligand[7,8] observed for various thorium(IV) complexes, some mixed ligand complexes of thorium(IV) derived from 4-[N-(2-hydroxy-1-naphthalidene)amino]antipyrinesemicarbazone (HNAAPS) and 4[N-(cinnamalidene)amino]antipyrinesemicarbazone are reported[8].

Transition metals complexes of amino acids, peptides and xylenol oranges in aqueous solution were studied by various techniques[9-14]. Potentiometry and UV-Vis spectrophotometry are the most widly used methods in the investigation of metal-peptide complexes[15]. Many analytical methods use molecular absorption spectrophotometry of coordination compounds for the determination of metal ions in solution.

Therefore, it has been decided to carry out an equilibrium study of the interaction of xylenol oranges with metal ions to determine stability of species formed. These complexes may serve to determine the interaction leading to metal promoted hydrolysis that this case can illustrate with investigation of structure of xylenol orange (Fig. 1)[11]. Also, the knowledge of the distribution of species with pH is a prerequisite for future kinetic studies[16].

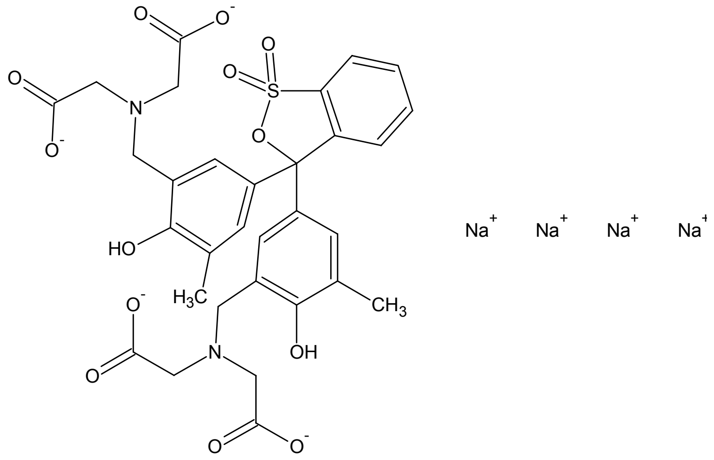

Fig. 1. Chemical structure of xylenol orange tetra sodium

This work deals with the study of Th(IV) complexes by xylenol orange and determining their stability constants at different temperature and constant ionic strength 0.1 mol dm^{-3} sodium perchlorate. The formation constants of the formed complexes have been compared with similar systems and interpreted. Some thermodynamic parameters were also calculated both for xylenol orange and for complexes at different temperatures.

EXPERIMENTAL

Xylenol orange tetra sodium salt ($C_{31}H_{28}N_2O_{13}SNa_4$) was obtained from Merck. The aqueous stock solutions of the ligand were freshly prepared daily. The NaOH solution was prepared from a titrisol solution (Merck) and its concentration was determined by several titrations with standard HCl. Perchloric acid, sodium perchlorate, thorium(IV) nitrate were purchased from Fluka as analytical reagent grade materials and used without further purification. Dilute perchloric acid solutions were standardized against standard NaOH solution. All the standard solutions were prepared using deionized and twice distilled water with specific conductance equal to (1.8 ± 0.1) $\mu\Omega^{-1}$ cm^{-1}. Ionic strength was adjusted to 0.1 mol dm^{-3} by addition of $NaClO_4$.

A Horiba pH-meter, M-12 was used for pH measurements. The hydrogen ion concentration was measured with an in gold UO 3234 glass electrode and in gold UO 3236 calomel electrode. Spectrophotometric titrations were performed on a UV-Vis Perkin Elmer, Lambda 25 double beam spectrophotometer from 200 to 350 nm and optical path 1.000 cm.

Measurements were carried out at 15, 20, 25, 30 and 35 ºC. The ionic strength 0.1 mol dm^{-3} adjusted with sodium perchlorate. The pH-meter was calibrated for the relevant H$^+$ concentration with solution of 0.01 mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm^{-3}). For this standard solution[17], we set -log [H$^+$] = 2.0. Junction potential corrections have been calculated from eqn. 1.

$$-\log [H^+]_{real} = -\log [H^+]_{measured} + a + b\,[H^+]_{measured} \qquad (1)$$

a and b were determined by measuring H$^+$ concentration for two different solutions of $HClO_4$ with sufficient $NaClO_4$ to adjust the ionic medium. Then formation constants of xylenol orange were measured with potentiometric method at 15, 20, 25, 30 and 35 ºC (Table-1).

TABLE-1
FORMATION CONSTANTS OF XYLENOL ORANGE IN DIFFERENT TEMPERATURE AND IONIC STRENGTH 0.1 mol dm^{-3} $NaClO_4$

T (K)	288.15	293.15	298.15	303.15	308.15
Ka_1	1.68E-3	1.93E-3	2.15E-3	2.36E-3	2.50E-3
Ka_2	7.41E-5	8.78E-5	1.00E-4	1.12E-4	1.22E-4
Ka_3	4.64E-6	5.45E-6	6.08E-6	6.86E-6	7.36E-6

25 mL Acidic solution of Th^{4+} in the concentrations range $5.0E^{-6}$ to $5.0E^{-5}$ mol dm^{-3} were titrated with an alkali solution of ligand containing a large excess of ligand (the ratios of metal ion to ligand 1:100). Ionic strength was maintained at 0.1 mol dm^{-3}, in the presence of $NaClO_4$. The -log $[H^+]$ and absorbance were measured after addition of a few drops of titrant and this procedure extended up to required -log $[H^+]$. During all the experiment, temperature was kept constant. Later, measuring was repeated with change of the temperature. A purified nitrogen atmosphere was maintained in the vessel during the titrations. In all cases, the procedure was repeated at least three times. The resulting average values are shown in the Table-3. log β_{111} and log β_{122} at different temperatures with ionic strength 0.1 mol dm^{-3} $NaClO_4$, were calculated.

RESULTS AND DISCUSSION

The complex $M_xH_yL_z^{(nx+y-z)}$ formed is characterized by its stoichiometry (x:y:z), where M and L represent the metal ion and ligand, respectively. To determine the stability constant of the complexation or the protonation, eqn. 2 is defined by β_{xyz}[18]:

$$xM^{n+} + yH^{+} + zL^{-} = M_xH_yL_z^{(nx+y-z)+} \quad (2)$$

$$\beta_{xyz} = [M_xH_yL_z^{(nx+y-z)+}]/([M^{+n}]^x[H^+]^y[L]^z) \quad (3)$$

The protonation constants of the xylenol orange have been used for computation of the stability constant, β_{xyz}, of the metal-ligand. The protonation constants of the xylenol orange have been extensively studied in different kinds of background electrolytes and the results were reported in the literature. To illustrate, there are xylenol orange compound in solution to four species: H_5XO, H_4XO, H_3XO and H_2XO. This assumption was confirmed by offering some other species, as mentioned before, that all were rejected by the computer program. In Fig. 2 the equilibrium distribution of various

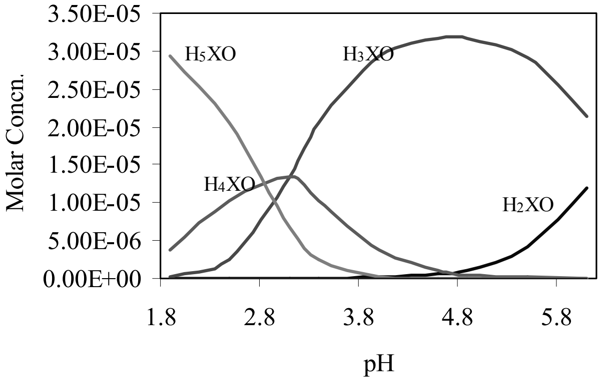

Fig. 2. Equilibrium distribution of the species xylenol orange system as a function of pH at 25 °C in ionic strength 0.1 mol dm^{-3} sodium perchlorate

species in xylenol orange system is shown as a function of pH. Where Ka_1, Ka_2 and Ka_3 are stepwise dissociation constants. Henderson's equations shows that, pH is a linear function of log $[H_5XO]/[H_4XO]$, log $[H_4XO]/[H_3XO]$ and log $[H_3XO]/[H_2XO]$ in acid and basic titrations, respectively. From the intercept of these equations, the values of Ka_1, Ka_2 and Ka_3 can be obtained, respectively. Because of K is varied by change of temperature, then we calculated them with changing of temperature (Table-1). In this work, the protonation constants of the xylenol orange have been determined using potentiometric techniques and calculated using a computer program which employs a least-squares method[18].

With increasing temperature, the dissociation constants are increased (Table-1) and this case shows that protonations of xylenol orange are endothermic. By using Gibs-Helmholtz equation, we can obtain thermodynamic parameters. Gibs-Helmholtz equation shows that, ln K is a linear function of 1/T that curves are given in Figs. 3-5. From the slope of this equation, the values of ΔH can be obtained and then ΔG and ΔS are calculated, consequently. In this work, ΔH, ΔG and ΔS are obtained for each step of dissociation of xylenol orange that results[19,20] are given in the Table-2.

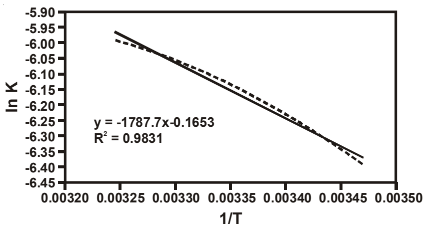

Fig. 3. Plot of ln Ka_1 *vs.* 1/T for first step of dissociation of xylenol

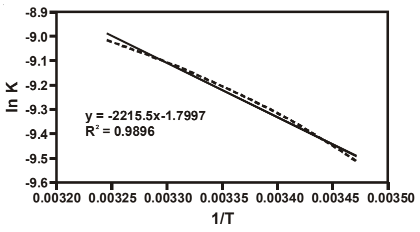

Fig. 4. Plot of ln Ka_2 *vs.* 1/T for second step of dissociation of xylenol

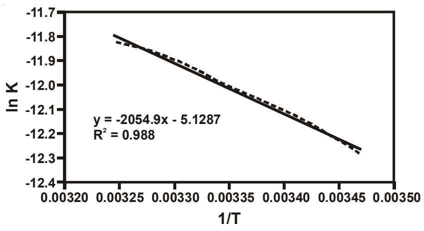

Fig. 5. Plot of ln Ka_3 *vs.* 1/T for third step of dissociation of xylenol

The data in Table-2 show that ΔG and ΔH approximately increase with increasing of steps of dissociation constants or decreasing of dissociation constants. This case shows that, the higher steps of dissociation are the difficult for xylenol orange. ΔS also decreases in higher steps of dissociation. This case emphasizes that higher steps of dissociation are more difficult.

TABLE-2
ΔG, ΔH AND ΔS VALUES FOR THREE STEPS OF IONIZATION OF XYLENOL ORANGE

Steps	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Ka_1	15.038	14.863	-1.374
Ka_2	22.783	18.419	-14.963
Ka_3	29.419	17.084	-42.640

The method of determination of the stability constant is based on the relation A = f (pH) on account of the high stability of the complexes studied. Absorbance, A and -log [H^+], were measured for a solution containing Th^{4+} with a large excess of xylenol orange. Treatment of the spectrophotometric data (each 1 nm) obtained during the titrations as a function of the H^+ concentration were conducted on the computer program. The program allows calculation of stability constant for different models of stoichiometries. The degree of refinement then guides to the choice between models. Considering the protonation constants of the ligand, in acidic pH the predominant species for complexation are H_3XO and H_4XO for xylenol orange (Fig. 2). In this case the spectrophotometric titration data were analyzed by using the absorbance of Th^{4+} with ligand at wavelengths in UV range that is given by

$$A = \varepsilon_{Th}[Th^+] + \varepsilon_{c1}[ThHXO] + \varepsilon_{c2}[ThH_2XO_2] + \varepsilon_{H_2XO}[H_2XO] + \varepsilon_{H_5XO}[H_5XO] \quad (4)$$

where ε_{Th}, ε_{c1} and ε_{c2} are the molar absorptivities of Th^{4+} and different species of ligand in acidic range, respectively. For the mass balance

$$F_{Th} = [Th^+] + [ThHXO] + [Th_2XO_2] \quad (5)$$

And if α_1 and α_0 be the fractions of the total concentration xylenol orange in the H_3XO and H_4XO, respectively.

$$\alpha_1 = \frac{[H_3XO]}{F_{tot}} \quad (6)$$

$$\alpha_0 = \frac{[H_4XO]}{F_{tot}} \quad (7)$$

where F_{Th} and F_{tot} are the total concentrations of Th and ligand, respectively. Substituting eqns. 3 and 5-7 into eqn. 6 gives the final equation for fitting. The method of determining $\varepsilon_{Th(IV)}$ was previously described[21] and its values at different wavelengths are used in this work. Using a suitable computer program[18] the data were fitted to the final equation for estimating the formation constant of eqn. 3. We used the Gauss-Newton non-linear least-squares method in computer program to refine the absorbance by minimizing sum of the squares error for eqn. 6

$$U = \Sigma (a_i - b_i)^2 \ (i = 1, 2, 3,) \quad (8)$$

where a_i is quasi-experimental and b_i is a calculated one. The computer program consisted of two different kind of fitting[21]. The final section of the species was based on both graphical and numerical methods, considering in addition the various statically criteria, *i.e.* sums of squared residuals, differences of F_{Th} (exp) and F_{tot} (exp) from those of calculated one[21].

Different models including MHL, MH_2L_2 and several polynuclear and protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were MH_2L, MHL_2 and ML_2. Values for some species were calculated by the program, but the species were not further considered because the estimated error in their formation constants is unacceptable and their inclusion does not improve the goodness of the fit.

The models finally chosen, formed by ThHXO and ThH_2XO_2, for xylenol orange, resulted in a satisfactory numerical and graphical fitting. The average values for various wavelengths, at different temperatures calculated for the stability constants are listed in Table-3.

TABLE-3
AVERAGE VALUES OF log β_{111} AND log β_{122} FOR DIFFERENT WAVELENGTHS AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS (I) 0.1 mol dm^{-3} ($NaClO_4$)

T (K)	288.15	293.15	298.15	303.15	308.15
log β_{111}	8.28	8.13	7.89	7.64	7.43
log β_{122}	17.09	16.64	16.64	16.49	16.33

With increasing temperature, the stability constants are decreased (Table-3) and this case shows that the stability constants are exothermic. Using of Gibs-Helmholtz equation, we can obtain thermodynamic parameters. Gibs-Helmholtz equation shows that, ln K is a linear function of 1/T that curves are given in Figs. 6 and 7. From the slope of this equation, the values of ΔH can be obtained and then ΔG and ΔS are calculated, consequently. In this work, ΔH, ΔG and ΔS are obtained for each step of formation of complex that results[19,20] are given in the Table-4.

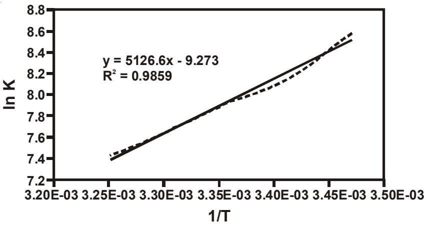

Fig. 6. Plot of formation constants of ThHXO *vs.* 1/T

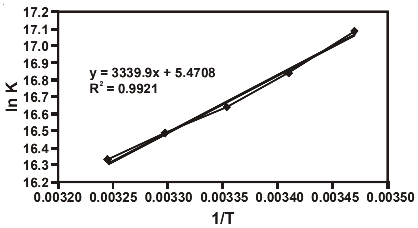

Fig. 7. Plot of formation constants of ThH_2XO_2 *vs.* 1/T

TABLE-4
ΔG, ΔH AND ΔS VALUES FOR FORMATION OF
COMPLEXES OF ThHXO AND ThH_2XO_2

Compounds	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
ThHXO	-19.636	-42.622	-77.095
ThH_2XO_2	-41.330	-27.768	45.486

The data in Table-4 were emphasized with stability constants of Table-3. Species of ThH_2XO_2 is much more stable than ThHXO at all temperatures.

Xylenol orange that studied in this work may coordinate Th(IV) *via* the O-donor groups. In the case of Th(IV)-XO system, the computer program suggests that the species MHXO and MH_2XO_2 are only 10 %. This assumption was confirmed by offering some other species, as mentioned before, that all were rejected by the computer program. In Fig. 8 equilibrium distributions of various species in Th-XO systems are shown as a function pH[22]. The calculations are based on the stability constant values given in Table-3. In the Th-XO system, ThHXO and ThH_2XO_2 are the dominant species in the pH = 3.4 (Fig. 8).

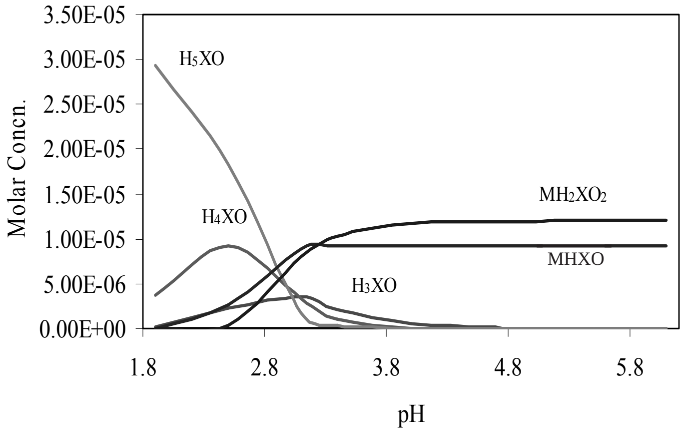

Fig. 8. Equilibrium distribution of the species Th-XO system as a function of pH at 25 ºC in ionic strength 0.1 mol dm^{-3} sodium perchlorate

Conclusion

These assumption have been confirmed by the finding that the stability constant values of ThH_2XO_2 specie are much more stable than those that formed by ThHXO at all temperatures and their log β_{122} are higher than those of HXO by about 9 log units. Thermodynamic parameters were confirmed this subject. There are some benzyl group in the ligand, the complexation of thorium(IV) by the ligand indicates influence benzyl group on the donor sites -COO^- and -OH in xylenol for complex formation, *i.e.* because benzyl group decreases the Lewis basicity and nucleophilicity donor sites. Also with increasing of temperature, the stability constants of ThHXO and ThH_2XO_2 were decreased (because formation of complexes is exothermic).

In this work, the study of interaction of thorium(IV) with xylenol orange was attempted in order to better understand the influence of the presence of a benzyl group in the stability of xylenol orange to bind thorium(IV), also influence heavy metals for complex formation.

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