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THERMODYNAMICS OF SOLVENT EXTRACTION OF THORIUM BY SOLUTIONS OF HTTA AND MIXTURES OF HTTA AND TBP

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ABSTRACT

The changes in free energy, enthalpy and entropy for the extraction of thorium by solutions of thenoyltrifluoroacetone (HTTA) and mixtures of solutions of HTTA and tri-*n*-butylphosphate (TBP), in three diluents, viz. cyclohexane, benzene and chloroform, were determined using the solvent extraction data obtained at different temperatures. From these data the thermodynamic parameters associated with the formation of $Th(TTA)_4 \cdot TBP$ in the respective organic diluents were evaluated. Trends in the enthalpy changes were attributed to different degrees of association of the diluents with themselves and with the solutes present in them.

INTRODUCTION

The synergistic enhancement in the extraction of metal ions is known to be strongly influenced by the diluents used, although the adduct species responsible for synergism remains the same in all the diluents. The synergism, using mixtures of β-diketones and neutral donors, was generally found [1] to decrease in the order: cyclohexane > hexane > carbon tetrachloride > benzene > chloroform. Different approaches have been pursued [2] to explain this order. Dielectric constant, polarity, interaction with neutral donors and water content are some of the factors advanced to explain the diluent behaviour. More recently, Akiba et al. [3—6] have successfully used the regular solution theory and attributed the effect to variations in the activity coefficients of the species involved in the equilibria, from one diluent to another.

Data on thermodynamic parameters associated with synergistic extraction, using different diluents, have not so far been reported. It was felt that such data may help in understanding the synergistic extraction behaviour including the diluent effect. In continuation of our earlier work on the synergistic extraction of thorium [7,8], extraction of thorium by solutions of HTTA and TBP, using the diluents cyclohexane, benzene and chloroform, was studied at different temperatures and the results obtained are described here.

EXPERIMENTAL

Materials

^{234}Th was separated [7] from nuclear grade uranium. HTTA (E. Merck, Germany) was kept under vacuum, over P_2O_5, for several hours before use. Stock solutions of HTTA in the required diluents were pre-equilibrated with dilute perchloric acid for several hours to allow hydration of HTTA. TBP was purified [9]. Analar chloroform was washed thoroughly with water. All other reagents used were of AR grade.

Procedure

The experimental procedure for the determination of distribution ratios of thorium is the same as described earlier [7]. The temperature was kept as desired by using a thermostated water bath, the temperature of which was maintained within ±0.1°C. 0.10 M perchloric acid was used as the aqueous medium for all the extraction experiments. Equilibrium aqueous [HTTA] was determined spectroscopically [10]. Equilibrium organic [HTTA] was calculated by subtracting the aqueous [HTTA] from initial organic [HTTA]. When cyclohexane was used as the diluent there was an appreciable transfer of HTTA to the aqueous phase. The distribution ratios of thorium (D) were then corrected for aqueous phase TTA complexing of thorium [11] and were normalised to the same organic [HTTA], for all the temperatures, assuming 4th power dependency of D on organic [HTTA]. The distribution ratios were measured in triplicate and the agreement between them was better than ±2%.

RESULTS

Extraction of thorium by solutions of HTTA

The extraction of Th(IV) from dilute perchloric acid medium by solutions of HTTA is represented as shown in eqn. (1).

$$\mathrm{Th}^{4+}_{(a)} + 4\,\mathrm{HTTA}_{(o)} \overset{K_A}{\rightleftharpoons} \mathrm{Th(TTA)}_{4_{(o)}} + 4\,\mathrm{H}^{+}_{(a)} \qquad (1)$$

The subscripts (a) and (o) refer to the species present in aqueous and organic media, respectively. The concentration equilibrium constant K_A is given by

$$K_A = \frac{[\mathrm{Th(TTA)_4}]\,[\mathrm{H^+}]^4}{[\mathrm{Th^{4+}}]\,[\mathrm{HTTA}]^4} = D_A\,\frac{[\mathrm{H^+}]^4}{[\mathrm{HTTA}]^4} \qquad (2)$$

where D_A is the distribution ratio of thorium. Using three diluents for HTTA, the distribution ratios of thorium were measured, at constant organic [HTTA] and aqueous [H$^+$], at different temperatures and the values obtained are given in Table 1. The D_A values are plotted against $1/T$ (Fig. 1) and the enthalpy changes for the equilibrium represented by eqn. (1) were

TABLE 1

Data on the distribution ratios of thorium obtained at different temperatures

Aqueous phase—0.10 M perchloric acid

[HTTA]/diluent	Distribution ratio (D_A) at			
	20°C	30°C	40°C	50°C
0.03 M/C_6H_{12}	2.99	2.88	3.22	4.05
0.03 M/C_6H_6	1.18	1.29	1.52	1.75
0.05 M/$CHCl_3$	0.385	0.552	0.808	1.10

calculated from these plots by using the relationship

$$\frac{\Delta \log D_A}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \tag{3}$$

The use of D_A in eqn. (3) in the place of K_A is justified since $D_A \propto K_A$ when [HTTA] and [H^+] are held constant [eqn. (2)]. The ΔG values for the equilibrium represented by eqn. (1) were calculated from log K_A values reported earlier [7] by using the relation

$$\Delta G = -2.303RT \log K_A \tag{4}$$

The ΔS values are obtained from the relationship

$$\Delta G = \Delta H - T \cdot \Delta S \tag{5}$$

The thermodynamic parameters thus obtained for the three diluents are given in Table 3.

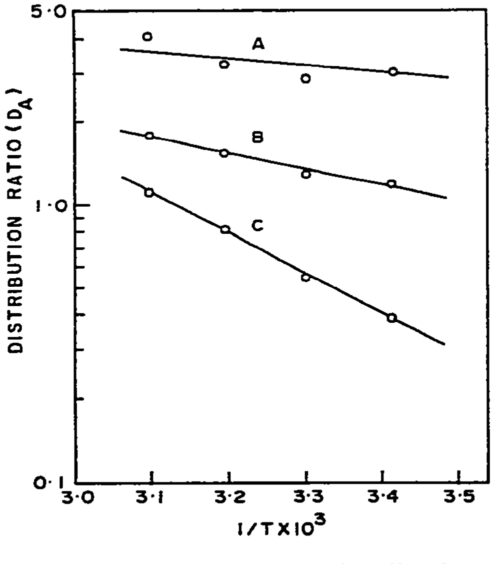

Fig. 1. Variation of the distribution ratio of thorium (D_A) with $1/T$. A, Cyclohexane—0.03 M HTTA; B, benzene—0.03 M HTTA; C, chloroform—0.05 M HTTA.

TABLE 2

Data on the distribution ratios of thorium obtained at different temperatures
Aqueous phase—0.10 M perchloric acid

[HTTA]/[TBP]/diluent	Distribution ratio at			
	20°C	30°C	40°C	50°C
0.002 M/0.005 M/C_6H_{12}	1.16	0.634	0.311	0.176
0.002 M/0.01 M/C_6H_{12}	2.01	1.01	0.517	0.311
0.01 M/0.001 M/C_6H_6	1.19	0.727	0.468	0.325
0.01 M/0.005 M/C_6H_6	5.69	3.69	2.39	1.61
0.05 M/0.002 M/$CHCl_3$	2.42	2.40	2.32	2.25
0.05 M/0.003 M/$CHCl_3$	6.92	6.65	6.17	6.63

Extraction of thorium by solutions of HTTA and TBP

The extraction of Th(IV) from dilute perchloric acid medium by solutions of HTTA and TBP is represented as shown in eqn. (6).

$$\mathrm{Th}^{4+}_{(a)} + 4\ \mathrm{HTTA}_{(o)} + \mathrm{TBP}_{(o)} \overset{K_{AB}}{\rightleftharpoons} \mathrm{Th(TTA)_4 \cdot TBP}_{(o)} + 4\ \mathrm{H}^{+}_{(a)} \qquad (6)$$

The concentration equilibrium constant K_{AB} is given by

$$K_{AB} = \frac{[\mathrm{Th(TTA)_4 \cdot TBP}]\,[\mathrm{H}^+]^4}{[\mathrm{Th}^{4+}]\,[\mathrm{HTTA}]^4[\mathrm{TBP}]} = D_{AB}\,\frac{[\mathrm{H}^+]^4}{[\mathrm{HTTA}]^4[\mathrm{TBP}]} \qquad (7)$$

TABLE 3

Thermodynamic data obtained for different equilibria (temperature = 25° C)

Solvent	ΔG (kcal mole^{-1})	ΔH (kcal mole^{-1})	ΔS (e.u.)
$\mathrm{Th}^{4+}_{(a)} + 4\ \mathrm{HTTA}_{(o)} \overset{K_A}{\rightleftharpoons} \mathrm{Th(TTA)_4 \cdot TBP}_{(o)} + 4\ \mathrm{H}^{+}_{(a)}$			
Cyclohexane	—3.72	0.87	15.4
Benzene	—3.07	2.56	18.9
Chloroform	—1.36	6.53	26.5
$\mathrm{Th}^{4+}_{(a)} + 4\ \mathrm{HTTA}_{(o)} + \mathrm{TBP}_{(o)} \overset{K_{AB}}{\rightleftharpoons} \mathrm{Th(TTA)_4 \cdot TBP}_{(o)} + 4\ \mathrm{H}^{+}_{(a)}$			
Cyclohexane	—12.00	—10.50	5.0
Benzene	—9.39	—7.89	5.0
Chloroform	—5.78	—0.52	17.6
$\mathrm{Th(TTA)_4}_{(o)} + \mathrm{TBP}_{(o)} \overset{\beta_{AB}}{\rightleftharpoons} \mathrm{Th(TTA)_4 \cdot TBP}_{(o)}$			
Cyclohexane	—8.28	—11.37	—10.4
Benzene	—6.32	—10.45	—13.9
Chloroform	—4.42	—7.05	—8.9

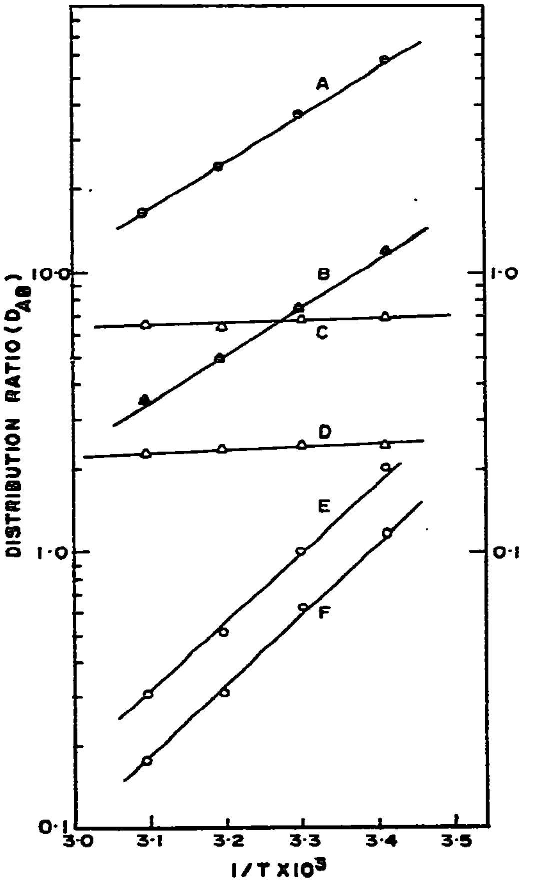

Fig. 2. Variation of the distribution ratio of thorium (D_{AB}) with $1/T$. A, Benzene—0.01 M HTTA—0.005 M TBP; B, benzene—0.01 M HTTA—0.001 M TBP; C, chloroform—0.05 M HTTA—0.003 M TBP; D, chloroform—0.05 M HTTA—0.002 M TBP; E, cyclohexane—0.002 M HTTA—0.01 M TBP; F, cyclohexane—0.002 M HTTA—0.005 M TBP.

where $D_{AB} = D - D_A$, when D is the observed distribution ratio of thorium with a solution of HTTA in the presence of TBP. Using the same three diluents for HTTA and TBP the D_{AB} values were measured at constant [HTTA], [TBP] and [H$^+$] at different temperatures and the values obtained are given in Table 2. The D_{AB} values are plotted against $1/T$ (Fig. 2) and the enthalpy changes for the equilibrium represented by eqn. (6) were calculated from these plots. The thermodynamic parameters for the equilibrium represented by eqn. (6) are included in Table 3.

Adduct formation in the organic phase

From eqns. (1) and (6) it can be shown that

$$\frac{K_{AB}}{K_A} = \beta_{AB} \tag{8}$$

where β_{AB} is the concentration equilibrium constant for the organic phase adduct formation equilibrium represented by eqn. (9).

$$Th(TTA)_{4(o)} + TBP_{(o)} \overset{\beta_{AB}}{\rightleftharpoons} Th(TTA)_4 \cdot TBP \qquad (9)$$

Thermodynamic data for this equilibrium were computed using the data obtained for the equilibria represented by eqns. (1) and (6) and they are also included in Table 3.

DISCUSSION

The data summarised in Table 3 show that the diluent used has an appreciable effect on the values of ΔG, ΔH and ΔS for all the equilibria. The effect of diluents on the enthalpy changes associated with the extraction process could be explained using Burger's [12] arguments. He has suggested that the overall enthalpy change (ΔH) in the extraction consists of the enthalpy changes associated with (a) the dehydration of the metal ion (ΔH_1), (b) the formation of the neutral extractable complex (ΔH_2), and (c) the dissolution of the neutral complex in the organic phase (ΔH_3). The magnitude as well as the sign of ΔH depends on the contributions from ΔH_1, ΔH_2 and ΔH_3. As the extraction using all the diluents is carried from the same aqueous medium, ΔH_1 remains unchanged. Similarly, as $Th(TTA)_4$ and $Th(TTA)_4 \cdot TBP$ are the only species involved in the extraction, respectively, with HTTA and mixtures of HTTA and TBP with all the diluents used, ΔH_2 also remains the same. ΔH_3, the enthalpy change associated with the dissolution of the bulky molecule $Th(TTA)_4$ or $Th(TTA)_4 \cdot TBP$ in the organic phase, in the absence of any appreciable interaction with the diluent, is endothermic, as work is required to disrupt the molecular arrangement present in the organic phase. This would primarily depend on the extent of intermolecular interactions existing in the diluent. In cyclohexane the dispersion forces [13] are the only cause of intermolecular interaction, whereas in benzene the presence of polarisable π electrons causes additional interactions. Chloroform, by virtue of having a potential site for hydrogen bonding [13], is expected to have the maximum interactions among the diluents studied. Thus the magnitude of ΔH_3 is expected to follow the order, cyclohexane < benzene < chloroform. The overall enthalpy change (ΔH) in the extraction of Th(IV) by solutions of HTTA alone is, however, endothermic in all the diluents used, its magnitude is highest in chloroform and least in cyclohexane as expected from the ΔH_3 contribution in these diluents. The main driving force for the extraction of Th(IV) by solutions of HTTA is the positive entropy change, mainly due to the liberation of water molecules from the hydration sphere of Th(IV).

The extraction of Th(IV) by mixtures of solutions of HTTA and TBP is exothermic with all the diluents, due to direct bonding of TBP to thorium ion, but even here the ΔH values follow the order expected from the ΔH_3 term for these diluents.

In the organic phase interaction between $Th(TTA)_4$ and TBP, the latter is directly bound with thorium to form $Th(TTA)_4 \cdot TBP$, thus making this reaction exothermic in all the diluents used. However, as more work is required to overcome the interaction between TBP and chloroform, the magnitude of ΔH is least in chloroform. Negative entropy changes observed with all the diluents are a result of more ordering due to the combination of $Th(TTA)_4$ and TBP.

Thus, the diluent effect in synergism can be qualitatively explained satisfactorily on the basis of the interactions of the diluents with themselves and with the solutes present in them. Quantitative data on these interactions would be highly useful in gaining a better understanding of the role of diluents in solvent extraction.

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