

Synergism in the extraction of scandium

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Abstract. Synergism in the extraction of scandium by a mixture of di-2-ethylhexyl phosphoric acid and a β -diketone has been studied. The nature of the extracted species has been investigated. The effect of temperature on extraction has been studied and synergism has been explained on the basis of thermodynamic parameters of the extraction process.

Keywords. Synergism; scandium; thermodynamic parameters.

1. Introduction

Synergism in the extraction of metals by a mixture of a β -diketone and alkyl phosphorus ester has evinced considerable interest. Irving and Edgington (1960, 1961) have formulated the conditions for synergic extraction. Synergism in the extraction by a mixture of an alkyl phosphoric acid and an alkyl phosphate has also been studied by several workers (Liem and Dyrssen 1966; Baes 1963; Marcus and Kertes 1969). In our studies on the extraction of indium, a profound synergism has been observed in the presence of a mixture of an alkyl phosphoric acid and a β -diketone (Sudersanan and Sundaram 1977). This type of synergism has not been studied to any extent. Similar results were also obtained in the case of europium by Pushparaja *et al* (1979). The nature of the complexes and the mechanism of extraction have been reported. In continuation of this work, results on the extraction of scandium are presented in this paper.

2. Experimental

Scandium in the form of ^{46}Sc obtained from the Isotope Group of our Centre was assayed by γ -counting using a single channel analyser. Di-2-ethylhexyl phosphoric acid, HDEHP (BDH LR) was purified to over 99% by the method of Peppard *et al* (1958). Thenoyl trifluoroacetone (HTTA) was of analytical grade (Koch Light Lab., Puriss). Benzene (BDH AR) was used as the diluent.

Extraction experiments were carried out by equilibrating the aqueous phase containing the metal and varying amounts of perchloric acid to maintain the acid concentration with an equal volume of the benzene phase containing HDEHP and/or HTTA in a thermostated mechanical shaker at $30 \pm 1^\circ \text{C}$ for about 8 hr to attain the required equilibrium. The two phases were then separated and assayed for scandium.

3. Results and discussion

Extraction of scandium by HDEHP was studied as a function of the concentrations of the extractants and perchloric acid. Figure 1 gives the plot of $\log D$ vs a_{HClO_4} , the activity being calculated from the activity coefficients obtained from literature (Parson 1959). The extraction reaction can be written as

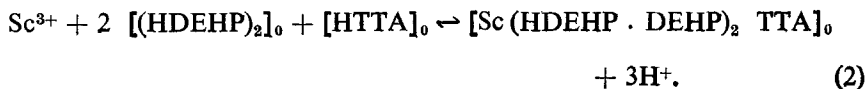


since HDEHP is known to exist as a dimer (Peppard *et al* 1958).

3.1. Scandium-HDEHP-HTTA system

The extraction of scandium by HTTA alone was found to be quite low under the experimental conditions although it has been found to extract scandium at lower acidities (Omori *et al* 1964; Shigematsu *et al* 1968). The extraction of scandium by a mixture of HDEHP and HTTA was studied as a function of the concentrations of perchloric acid, HDEHP and HTTA to investigate the nature of the extracted species. The results are presented in figure 2. The extraction was higher in the presence of β -diketone. The distribution ratio for the synergic species was calculated by subtracting the contribution due to HDEHP chelate alone. The plot of $\log D_{\text{syn}}$ vs $\log a_{\text{HClO}_4}$ (figure 2) gave a slope of about three indicating that three hydrogen ions are involved in the extraction process. The plot of $\log D_{\text{syn}}$ vs $\log [(\text{HDEHP})_2]_0$ at a constant concentration of HTTA and acid gave a slope of about 1.5 while the slope of the plot of $\log D_{\text{syn}}$ vs $\log [\text{HTTA}]_0$ at a constant concentration of HDEHP was one. The slope of the plot of the overall distribution ratio as a function of $\log [(\text{HDEHP})_2]_0$ was about two. Non-integral values for slopes are often obtained in extractions with alkyl phosphoric acid (Mason *et al* 1970).

The extraction of the mixed chelate can be described by



The equilibrium constants for the reactions described by eqs (1) and (2) can be written as

$$K'_{03} = D [\text{H}]^3 [(\text{HDEHP})_2]_0^{-3} \quad (3a)$$

$$\text{and } K'_{12} = D_{\text{syn}} [\text{H}]^3 [\text{HTTA}]_0^{-1} [(\text{HDEHP})_2]_0^{-2}. \quad (4a)$$

The experimental values of slopes obtained for the variation of HDEHP were 2.5 and 1.5 for the reactions of (1) and (2) respectively. These values were lower than

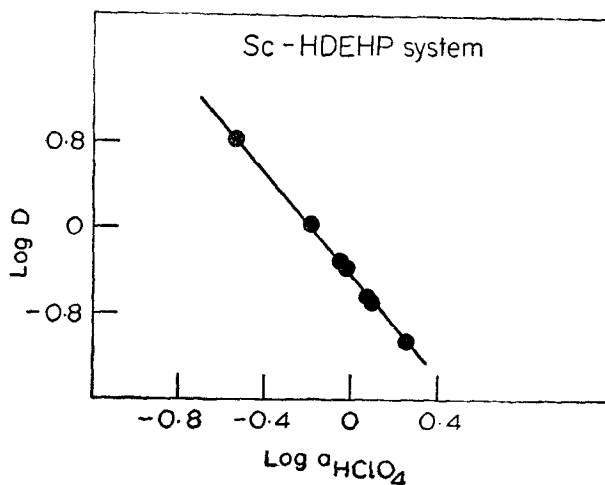


Figure 1. Plot of $\log D$ vs $\log a_{\text{HClO}_4}$.

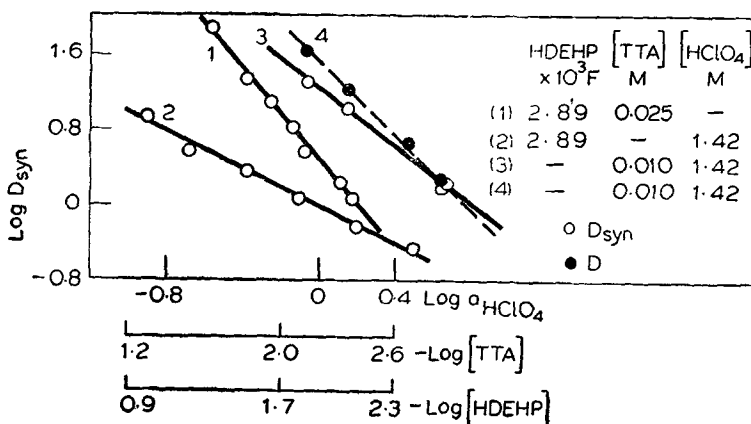


Figure 2. Plot of $\log D_{\text{syn}}$ vs \log (variant).

the expected values. Similar discrepancies in slope values are quite common for systems involving alkyl phosphoric acid. Several cases have been reported by Peppard (1966) where he represents the reaction on the basis of the experimental data without intent to imply a proved structure of the extracted entity. Hence for the calculations of the equilibrium constants, the experimental values were used. The equilibrium constants on this basis can be written as

$$K_{03} = D [H]^3 [(HDEHP)_2]_0^{-2.5} \tag{3b}$$

and
$$K_{12} = D_{\text{syn}} [H]^3 [HTTA]_0^{-1} [(HDEHP)_2]_0^{-1.5} . \tag{4b}$$

The values of D_{syn} were obtained (table 1) by subtracting the distribution ratio in the presence of HTTA or HDEHP from

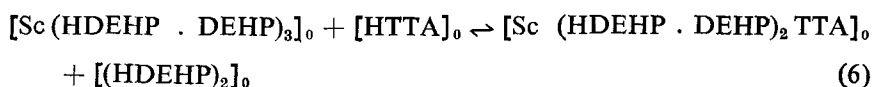
$$D_{\text{syn}} = D - D_{\text{HDEHP}} . \tag{5}$$

Table 1. Effect of temperature on the extraction of scandium by HDEHP and HTTA.

a_{HClO_4}	$\log D$	$\log D_{\text{syn}}$	Temp °C	$\log K^*$	$-\Delta G$ kcal
HDEHP = 2.89×10^{-3} F; HTTA = 0.0 M					
1.28	-0.02	..	13.0	6.65	8.7
1.28	-0.52	..	26.5	6.15	8.4
1.28	-0.83	..	35.0	5.84	8.2
1.28	-1.02	..	39.5	5.65	8.1
1.28	-1.17	..	51.0	5.50	8.2
HDEHP = 2.89×10^{-3} F; HTTA = 0.01 M					
0.85	1.18	1.04	9.0	6.64	8.6
0.85	1.08	0.94	12.0	6.54	8.5
0.85	0.81	0.68	20.0	6.28	8.4
0.85	0.66	0.55	26.5	6.15	8.4
0.85	0.49	0.42	35.0	6.01	8.5
1.08	0.93	0.80	9.0	6.71	8.7
1.08	0.87	0.77	12.0	6.68	8.7
1.08	0.62	0.52	20.0	6.43	8.6
1.08	0.25	0.18	35.0	6.09	8.6
1.08	0.14	0.09	39.5	5.99	8.6
1.28	0.73	0.61	9.0	6.74	8.7
1.28	0.66	0.56	12.0	6.69	8.7
1.28	0.47	0.39	20.0	6.52	8.7
1.28	0.23	0.18	26.5	6.31	8.6
1.28	0.06	0.00	35.0	6.13	8.6
1.28	-0.02	-0.07	39.5	6.06	8.7
HDEHP = 2.89×10^{-3} F; HTTA = 0.02 M					
1.28	0.91	0.86	13.0	6.68	8.7
1.28	0.67	0.62	20.0	6.45	8.7
1.28	0.29	0.26	35.0	6.08	8.6
1.28	0.21	0.18	39.5	6.01	8.6
1.28	0.05	0.02	50.5	5.85	8.7
HDEHP = 2.89×10^{-3} F; HTTA = 0.05 M					
1.28	1.21	1.18	13.0	6.61	8.7
1.28	1.00	0.98	20.0	6.41	8.6
1.28	0.88	0.87	26.5	6.30	8.6
1.28	0.60	0.59	39.5	6.02	8.6
1.28	0.43	0.42	50.0	5.85	8.7

* $K = D [\text{H}]^3 [\text{HDEHP}]^{-2.5}$ for parent chelates and
 $= D_{\text{syn}} [\text{H}]^3 [\text{HDEHP}]^{-1.5} [\text{HTTA}]^{-1}$ for mixed complexes.

Since the distribution ratio in the presence of HTTA is negligible, D_{HTTA} can be neglected. The value of D_{HDEHP} was estimated from the equilibrium constants or it can be estimated from the studies in the presence of HDEHP alone. The free energy, enthalpy and entropy changes for the extraction process were evaluated on the formality scale from the equilibrium constants calculated at different temperatures. Since D_{syn} is proportional to K_{12} , $\log D_{\text{syn}}$ was plotted as a function of $1/T$ for various concentrations of HTTA and HDEHP alone. The slopes for the various plots (figure 3) were nearly the same for the synergic species and ΔH was calculated as -9.7 kcal. Values of equilibrium constants calculated both on the basis of (3a) and (4a) or (3b) and (4b) are presented in table 2. The values of \log (equilibrium constants) calculated on the basis of (3b) or (4b) are uniformly higher by 1.27 log units because of the change in the exponent of HDEHP. However, the general conclusions regarding the nature of the extraction process are the same. The higher (negative) value of ΔS in the case of parent chelate may be due to the formation of a symmetrical molecule which is not statistically favourable. Since the thermodynamic equations are additive, the synergic reaction can be written as



by subtracting eqn. (1) from (2). Similarly the thermodynamic parameters for the synergic system were evaluated by subtraction of the values for the above reactions. The value of ΔG is almost zero indicating the synergic species to be as stable as the

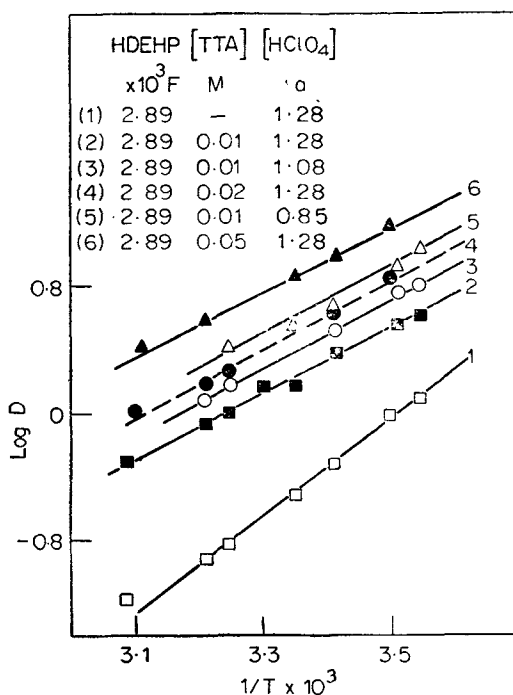


Figure 3. Scandium-HDEHP-TTA system; effect of temperature.

Table 2. Values of thermodynamic parameters (temp. 303 K; formality scale).

System	log (equil. const.)		$-\Delta G$ K cal.		$-\Delta H$	$-\Delta S$ cal/deg/mole	
	exp 2.5*	exp 3†	exp 2.5*	exp 3†	K cal	exp 2.5*	exp 3†
Parent chelate	6.1	7.4	8.5	10.3	-14.2	-19	-13
Mixed chelate	~6.1	~7.4	~8.6	~10.3	-9.7	-4	+2
Synergic system	~0.0	~0.0	~0.0	~0.0	4.5	+15	+15

* On the basis of 2.5 for the exponent of HDEHP for parent and 1.5 for mixed chelate.

† On the basis of 3 for the exponent of HDEHP for parent and 2 for mixed chelate.

parent chelate. A value of 4.5 kcal for ΔH indicates an endothermic reaction which is energetically unfavourable compared to other processes for which the values are negative. But this is compensated by a large change of 15 cal/deg/mole for ΔS which makes the mixed chelate as stable as the parent chelate. The increased stability is made possible by the highly favourable entropy change for the reaction which offsets the unfavourable enthalpy change. Similar results have been observed in our studies on indium (Sudersanan and Sundaram 1977), hafnium and europium (Pushparaja and Sudersanan 1978; Pushparaja *et al* 1979) and uranium-TTA adducts with tributyl phosphate, tri-*n*-octyl phosphine oxide, diphenyl and dibutyl sulfoxides (Subramanian and Pai 1970). Israeli (1964) also observed a similar synergic effect in the case of mixed chelates of EDTA and NTA. The favourable entropy change may be due to the introduction of compact HTTA molecules in the chelate which provides an unsymmetrical charge density distribution around the central metal ion.

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