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Synergism in the extraction of lanthanides, copper and thorium in presence of HTTA and antipyrine

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Abstract. Synergism in the extraction of lanthanum, europium, lutetium, copper and thorium has been studied using a mixture of HTTA and 2,3-dimethyl, 1-phenyl pyrazol-5-one (antipyrine). Synergism was observed in all the cases except copper. The nature of extracted species has been determined on the basis of log-log plots and the equilibrium constants for the adducts have been evaluated. Antipyrine has been found to be a good donor comparable in strength to other alkylphosphorus donors.

Keywords. Synergism; extraction of metals; HTTA; antipyrine.

1. Introduction

Studies on the extraction of uranium with a mixture of a β-diketone and antipyrine (2,3-dimethyl, 1-phenyl pyrazol-5-one) indicated the potentialities of antipyrine as a synergist (Malhotra *et al* 1984). Antipyrine is of considerable importance in medicine and other substituted pyrazolones are also attracting attention as β-diketones in extraction studies. In order to investigate the usefulness of antipyrine as a synergist, extraction of metal ions having different valence states, such as lanthanum, europium, lutetium, copper and thorium was studied from benzene media, the results of which are reported in this paper.

2. Experimental

Extraction experiments were carried out at 30°C at an ionic strength of 0·5 using sodium chloride. The extraction procedure has been described earlier (Malhotra *et al* 1984). The metal ions were estimated spectrophotometrically using thoron for thorium, arsenazo III for rare earths and diethyldithiocarbamate for copper using standard methods.

3. Results and discussion

In order to study the extraction behaviour of trivalent lanthanides, extraction of lanthanum, europium and lutetium as representatives of light, middle and heavy rare

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earths was studied. The pH was maintained at 4·2 and the distribution ratio was measured as a function of concentration of HTTA and antipyrine APY.

3.1 *Rare earths-HTTA-APY system*

Extraction of La, Eu and Lu with HTTA was quite low but addition of APY resulted in considerable enhancement in the extraction. The results for the extraction of La are shown in figure 1. The concentration of HTTA was varied keeping pH constant at 4·2 and $[\text{APY}]_{tot}$ at 0·008 M. The concentration of APY was also varied keeping HTTA constant at 0·02 M. The concentration of HTTA in the organic phase was calculated taking into account its partition coefficient of 54 (Sekine *et al* 1973). The concentration of $[\text{APY}]_0$ was calculated taking into account the partition coefficient of 0·525 and *pK* of 1·38 which were determined in a separate series of experiments. The plots of log *D* vs log $[\text{HTTA}]_0$ resulted in a straight line with a slope of 2·6 while that of log *D* vs log $[\text{APY}]_0$ resulted in a curve with the slope changing from zero to two. The results indicated the formation of an adduct having one to two molecules of APY. The data were analysed to evaluate the nature of the adduct.

The distribution ratio, *D* can be written as

$$D = \frac{[\text{La A}_3]_0 + [\text{La A}_3\ \text{APY}]_0 + [\text{La A}_3\ (\text{APY})_2]_0 + \ldots\ldots}{[\text{La}^{+3}]} \tag{1}$$

where A represents the anion of HTTA. Expressing (1) in terms of equilibrium constants of the adducts and on rearranging, we get

$$F_0 = \frac{D[\text{H}^+]^3}{[\text{HA}]_0^3} = \text{K}_{30} + \text{K}_{31}[\text{APY}]_0 + \text{K}_{32}\,[\text{APY}]_0^2, \tag{2}$$

where K_{3n} represents the equilibrium constant for the formation of $[\text{La A}_3\ (\text{APY})_n]_0$. Hence a plot of F_0 vs $[\text{APY}]_0$ can be used to evaluate the equilibrium constants for adduct formation. The plot resulted in a smooth curve (figure 1), which was utilised to calculate equilibrium constants summarised in table 1.

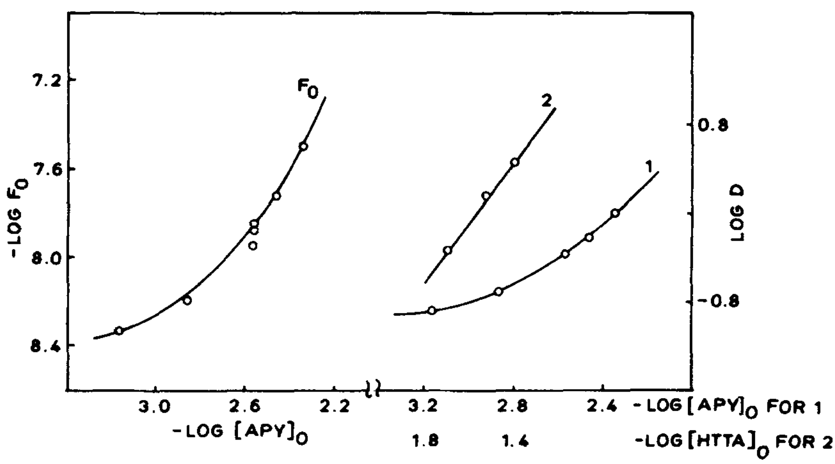

Figure 1. La-HTTA-APY system: log-log plots.

Table 1. Values of equilibrium constants.

Metal	μ	log equilibrium constant K_{30}	K_{31}	K_{32}	K_1^*	K_2^*
La(III)	0·5	−8·25	−6·00	−2·92	2·52	6·56
Eu(III)	0·5	−8·30	−3·87	−0·31	4·43	7·99
Lu(III)	0·5	−7·05	−2·24	1·60	4·81	8·65
Th(IV)	1·0	1·10*	6·60†	—	5·50	—

* log K_{40}; † log K_{41}.

Similar experiments were carried out using europium and lutetium and the results indicated the formation of two adducts. The values of equilibrium constants are summarised in table 1. Earlier studies on synergism in the extraction of europium (Sudersanan and Sundaram 1981a, b) with various donors indicated the formation of a diadduct with alkylphosphorus donors and sulphoxides while a monoadduct was indicated with nitrogen donors. The formation of both the adducts is indicated with all the three metals reported here. This is in agreement with the observation that antipyrine is intermediate in donor strength between nitrogen donors and alkylphosphates, as indicated by the extent of synergism.

The adduct formation constant K_n^* represented by

$$MA_3 + nS \overset{K_n^*}{\rightleftharpoons} MA_3\,S_n \tag{3}$$

where S is a donor, was also evaluated as $K_n^* = K_{3n}/K_{30}$. The values are summarised in table 1 and increase in the order La < Eu < Lu, which is in agreement with the increasing ionic potential of the metal ions. The equilibrium constants as well as the adduct formation constants increase with increase in atomic number indicating a greater separation factor between individual rare earths in the case of synergistic systems compared to β-diketones alone.

3.2 *Copper-HTTA-APY system*

Investigations were also extended to copper as a representative of divalent metal ions. Extraction of copper with HTTA both in the presence and absence of APY indicated that the enhancement in extraction was not significant. A comparative study was also made using TOPO, TPPO and TBP and the absence of appreciable synergism in all the cases indicated that the coordination number for copper did not change to a value higher than four in presence of moderate concentrations of the donor.

3.3 *Thorium-HTTA-APY system*

Synergism in the presence of APY was also investigated in the case of thorium, a tetravalent element. The distribution ratio was measured as a function of pH and concentration of HTTA and APY in 1·0 M sodium chloride. The plots of log D vs log $[\text{HTTA}]_0$ and log $[\text{APY}]_0$ at a pH of about 1·10 resulted in straight lines having slopes of 4 and 1 respectively indicating the formation of Th (TTA)$_4$ APY. The equilibrium constant was evaluated as $10^{6.6}$. The equilibrium constant for the extraction of thorium by HTTA alone was estimated at $10^{1.1}$ and hence log K_1^* was calculated as $10^{5.5}$ indicating synergism to be quite pronounced. The coordination number of thorium is likely to increase to nine as in the case of other donors like TBP, TOPO etc.

The above results indicate the suitability of antipyrine as a neutral donor in extraction studies. It has advantages over other donors, being a compound with high water solubility and being equally effective in causing synergism to the extent observed with neutral donors. In view of its low cost and easy availability it has potential applications in the extractive separation of metal ions. A separation of thorium and the rare earths is of interest since they occur together. The results indicate that they can be separated easily and the separation factor of lighter rare earths is enhanced by the use of synergistic systems.

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