

## Synergism in the extraction of cerium using nitrogen-base donors

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**Abstract.** Synergism in the extraction of cerium in presence of a mixture of a  $\beta$ -diketone and nitrogen donors like pyridine, 2,4-dimethylpyridine, quinoline and 8-nitroquinoline has been investigated. The nature of the extracted species has been investigated and the equilibrium constants for adduct formation have been calculated. Synergism increased in the order 8-nitroquinoline < pyridine  $\approx$  quinoline < 2,4-dimethyl pyridine.

**Keywords.** Synergism ; cerium ; extraction ; nitrogen base donors.

### 1. Introduction

Synergism in the extraction of metals has attracted considerable interest, most of the studies relating to the use of a mixture of a  $\beta$ -diketone and a neutral organophosphorus ester (Sekine and Hasegawa 1977; Marcus and Kertes 1969). Nitrogen donors have been used as synergists to a much lesser extent compared to alkylphosphates. Synergism in the extraction of cerium using phosphine oxides and sulfoxides has been reported (More *et al* 1979) from these laboratories. In continuation of this work, synergism in the extraction of cerium using a mixture of 4 : 4 : 4 trifluoro 1-(2-naphthyl) 1 : 3 butanedione and heterocyclic nitrogen donors is presented here.

### 2. Materials and methods

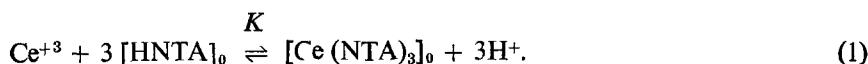
Cerium, obtained in the form of  $^{141}\text{Ce}$  from the Isotope Group of this Centre was assayed by  $\gamma$ -counting using a thallium activated sodium iodide  $\gamma$ -scintillation counter (Electronics Corporation of India, Hyderabad). 4 : 4 : 4 trifluoro-1-(2-naphthyl) 1 : 3 butanedione (K and K Labs) was used as a solution in carbon tetrachloride (BDH, AnalaR). Pyridine (BDH, AnalaR), 2 : 4 dimethyl pyridine (Hopkins and Williams), quinoline (Koch-Light Lab.) and 8-nitroquinoline (BDH) were used as synergists.

Extraction experiments were carried out by equilibrating 10 ml of the aqueous phase containing the metal (of the order of  $10^{-5}$  M in the final solution), sodium perchlorate to maintain the ionic strength at 1.0, acetic acid ( $\sim 0.034$  M) to maintain the pH with an equal volume of carbon tetrachloride containing the extractant and the neutral donor, for about 5 hr which was sufficient for equilibration. All experiments were carried out at  $25 \pm 1^\circ$  C. The pH of the aqueous phase was measured with a Beckman Expandomatic SS-2 pH meter. Corrections for the background activity were made.

### 3. Results and discussion

#### 3.1. Cerium HNTA system

Extraction of cerium (III) using 4 : 4 : 4-trifluoro 1-(2-naphthyl) 1 : 3 butanedione (HNTA) was studied as a function of pH and concentration of HNTA, which indicated the extraction of  $\text{Ce}(\text{NTA})_3$  represented by



The equilibrium constant  $K$  for the above reaction was determined as  $1.38 \times 10^{-11}$ .

#### 3.2. Cerium-HNTA-Pyridine system

Extraction of cerium was studied using a mixture of HNTA and pyridine (Py) at different pH and concentrations of HNTA and Py. The results are presented in figure 1. The plot of  $\log D$  vs  $\log [\text{HNTA}]_0$  resulted in a straight line with a slope of three. The reaction of pyridine with hydrogen ions and the partition coefficient ( $P_{\text{py}}$ ) of pyridine were considered to calculate the concentration of pyridine in the organic phase given by

$$[\text{Py}]_0 = \frac{P_{\text{py}} [\text{Py}]_{\text{tot}}}{\{1 + K_B^{-1} [\text{H}] + P_{\text{py}}\}}, \quad (1)$$

where  $K_B$  is the equilibrium constant of the reaction represented as

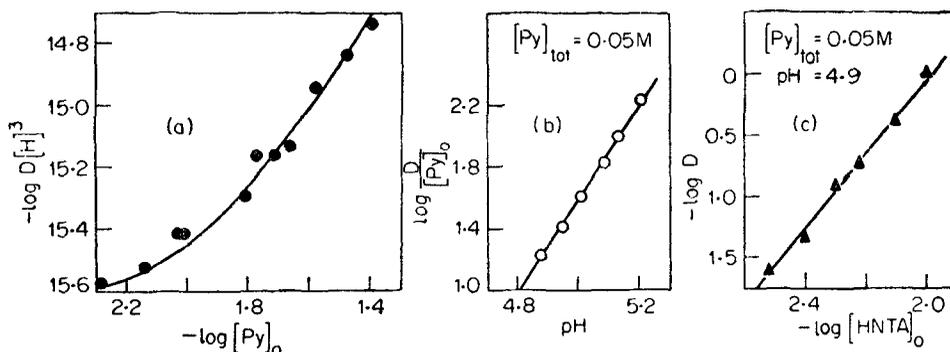
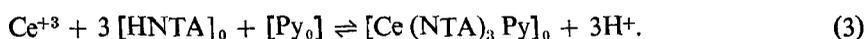


Figure 1. Cerium-HNTA-pyridine system. (a) Plot of  $\log D [\text{H}]^3$  vs  $\log [\text{Py}]_0$ . (b) Plot of  $\log D/[\text{Py}]_0$  vs pH. (c) Plot of  $\log D$  vs  $\log [\text{HNTA}]_0$ .

The values of 2.64 for  $P_{py}$  reported in benzene media (Hirose and Tanaka 1976) and 5.39 for  $pK_B$  (Smith and Martell 1975) were used for the present calculations. The plot of  $\log D$  vs  $\log [HNTA]_0$  resulted in a straight line with slope three suggesting the coordination of three molecules of HNTA with cerium. Since the pH also changed, it was not possible to plot  $\log D$  as a function of  $\log (Py)_0$  and hence the auxiliary function  $\log D [H]^3$  was plotted as a function of  $\log (Py)_0$  which resulted in a curve (figure 1) with the slope changing from 0 to 2 due to the formation of  $Ce(NTA)_3Py$  and  $Ce(NTA)_3(Py)_2$  though predominantly  $Ce(NTA)_3Py$ . Hence the reaction leading to the formation of the synergic species can be written as



The equilibrium constant  $K_{syn}$  is given by

$$K_{syn} = D'[H]^3[HNTA]_0^{-3}, \quad (4)$$

where  $D' = D[Py]_0^{-1}$ . (5)

The plot of  $\log D[Py]_0^{-1}$  as a function of pH resulted in a straight line having a slope of three indicating the liberation of three hydrogen ions in accordance with equation (3). The value of  $K_{syn}$  was calculated as  $5 \times 10^{-8}$ . The equilibrium constant was also calculated from

$$D/D_0 = \frac{[Ce(NTA)_3]_0 + [Ce(NTA)_3Py]_0}{[Ce(NTA)_3]_0}, \quad (6)$$

or  $\left(\frac{D}{D_0} - 1\right) [Py]_0^{-1} = K^*$ . (7)

The value of  $D_0$  in the absence of pyridine was calculated from the equilibrium constant of  $1.38 \times 10^{-11}$  for  $Ce(NTA)_3$  system. The function of equation (7) was practically constant indicating the predominance of the first adduct. The second adduct might however be formed at higher concentrations of pyridine as indicated by an increase in the values.  $K^*$  was calculated as  $3.5 \times 10^3$ .

### 3.3. Cerium-HNTA-Quinoline system

Extraction of cerium in the presence of another heterocyclic amine, quinoline ( $Q$ ), was studied as a function of pH and the concentrations of  $[HNTA]_0$  and  $[Q]_0$ . The  $pK_B$  was taken as 4.97 (Smith and Martell 1975) and the partition coefficient as  $10^{1.20}$  (Leo *et al* 1971). The concentration of quinoline in the organic phase was calculated as in the case of pyridine. Since quinoline was present mostly as unprotonated, the concentration of quinoline in the organic phase was almost comparable to the initial concentration. Extraction of cerium by quinoline alone was negligible.

The plots of  $\log D$  vs pH,  $\log [HNTA]_0$  resulted in straight lines of slope three. From the variation of  $\log D$  vs  $\log [Q]_0$  the number of quinoline molecules in the synergic species was found as one. The equilibrium constant  $K_{syn}$  was calculated as  $3.6 \times 10^{-8}$  and was nearly the same as in the case of pyridine system. The synergic stability constant  $K^*$  was calculated as  $2.63 \times 10^3$ .

### 3.4. Cerium-HNTA-2 : 4 Dimethyl pyridine system

With a view to understand the effect of substituents on the synergic extraction of cerium, nitrogen donors which are electron-donating or withdrawing were also studied. 2 : 4 dimethyl pyridine (DMP) has been used since the electron density is higher on the nitrogen atom because of the electron releasing tendency of methyl groups and 8-nitroquinoline (NQ) as electron-withdrawing group.

Extraction of cerium by DMP alone was negligible whereas it increased in the presence of HNTA. The plot of  $\log D$  vs  $\log [\text{HNTA}]_0$  resulted in a straight line with slope three. The plot of  $\log D$  vs pH resulted in a straight line having a slope of about four and of  $\log D$  vs  $\log [\text{DMP}]_{\text{tot}}$  resulted in a curve. These results suggested the mechanism of extraction to be similar to that of the pyridine system.

The pK values of 6.86 for DMP (Perrin 1965) and the partition coefficient of 20.5 reported (Hirose and Tanaka 1976) in some solvents were used for calculating the concentration of DMP in the organic phase. The plot of  $\log D$  vs  $[\text{DMP}]_0$  was modified taking into account the variation of  $[\text{DMP}]_0$  with pH  $\log D (\text{DMP})_0^{-1}$  plotted as a function of pH resulted in a straight line with a slope of about three indicating the participation of three hydrogen ions in the extraction reaction.

The extraction mechanism can be written as



with the equilibrium constant  $K_{\text{syn}}$  calculated as  $8.5 \times 10^{-7}$ . The synergic stability constant given by

$$K^* = \frac{[\text{Ce}(\text{NTA})_3\text{DMP}]_0}{[\text{Ce}(\text{NTA})_3]_0[\text{DMP}]_0}, \quad (9)$$

was calculated as  $6.17 \times 10^4$ . These results indicate that a greater stability of the adduct results from a greater donor strength of nitrogen in the presence of electron releasing groups like methyl group.

### 3.5. Cerium-HNTA-8-nitroquinoline system

Synergism in the extraction of cerium by 8-nitroquinoline (NQ) was also studied in order to investigate the influence of an electron-withdrawing group. Experiments were carried out in a similar manner and the plots of  $\log D$  vs pH,  $\log [\text{HNTA}]_0$  and  $\log [\text{NQ}]_0$  resulted in straight lines with slopes of 3, 3 and 0.6 respectively indicating the adduct of the type  $\text{Ce}(\text{NTA})_3\text{NQ}$ . The extraction was much less than that in the case of quinoline as indicated by the pH range of extraction.

The partition coefficient of NQ is considered high from a comparison with the value of  $10^{1.40}$  in octanol (Leo *et al* 1971). The dissociation constant (Perrin 1965) of  $10^{-2.55}$  indicates that NQ is present as unprotonated under the present experimental conditions and hence the concentration of NQ in the organic phase can be assumed as equal to the initial concentration. An attempt was also made to correct the measured distribution ratio for extraction due to HNTA alone using

$$D_{\text{syn}} = D - D_{\text{HNTA}}, \quad (10)$$

The plots for the variation of pH and  $\log (\text{HNTA})_0$  resulted in straight lines parallel to the corresponding plots of  $\log D$  while the slope of the straight line for the variation of  $[\text{NQ}]_0$  increased to about 1.0 indicating the presence of one molecule of NQ in the adduct. Since the extent of synergism was less, correction for extraction due to HNTA alone was significant in this case. The equilibrium constant,  $K_{\text{syn}}$ , was calculated as  $2.5 \times 10^{-9}$  and  $K^*$  as  $1.8 \times 10^2$  indicating the presence of an electron-withdrawing group to reduce considerably the stability of the adduct.

Synergism in the case of extraction with pyridine bases was much less compared to those observed with sulfoxides and phosphine oxides (More *et al* 1979). In the case of nitrogen donors, the order of synergism correlates with the basicity and steric effects of the methyl group. In the present case, the order observed as 2 : 4 dimethyl pyridine > pyridine  $\approx$  quinoline > 8-nitroquinoline correlates well with the basicity effect on the nitrogen atom (Akaiwa and Kawamoto 1967).

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### References

- Akaiwa H and Kawamoto H 1967 *J. Inorg. Nucl. Chem.* **29** 1345  
Hirose K and Tanaka M 1976 *J. Inorg. Nucl. Chem.* **38** 2285  
Leo A, Hansch C and Elkins D 1971 *Chem. Rev.* **71** 525  
Marcus Y and Kertes A S 1969 *Ion exchange and solvent extraction of metal complexes* (London : Wiley-Interscience)  
More A K, Sudersanan M and Sundaram A K 1979 *Indian J. Chem.* (in press)  
Perrin D D 1965 *Dissociation constants of organic bases in aqueous solution* (London: Butterworths)  
Sekine T and Hasegawa Y 1977 *Solvent extraction chemistry* (New York: Marcel Dekker)  
Smith R E and Martell A E 1975 *Critical stability constants* (New York: Plenum Press).