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Ion-Pair Extraction of Tetravalent Plutonium from Hydrochloric Acid Medium Using Crown Ethers

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Abstract. Ion-pair extraction behaviour of plutonium (IV) from varying concentrations of HCl solution was studied employing crown ethers (benzo-15-crown-5 (B15C5), 18-crown-6, (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6, (DC18C6), dibenzo-24-crown-8 (DB24C8) and dicyclohexano-24-crown-8 (DCH24C8)) in nitrobenzene as the extractant. Ammonium metavanidate was used as the holding oxidant in the aqueous phase and the conditions necessary for the quantitative extraction of the tetravalent ion were found. The co-extraction of species of the type $[HL^+]\cdot[HPu(Cl)_6^-]$ and $[HL^+]_2\cdot[Pu(Cl)_6^{2-}]$ as ion-pairs (where L represents the crown ether) is suggested.

Key words: Crown ethers, nitrobenzene, plutonium (IV), solvent extraction.

1. Introduction

The discovery of cyclic polyethers, commonly known as crown ethers, has enabled the design and synthesis of cation-specific ionophores exhibiting high complex formation constants as well as high selectivities for a very large number of cations [1–3]. In fact, the chemistry of these ligands has opened up new frontiers in the co-ordination behaviour of metal ions, allowing them to be applied to such diverse processes as isotope separations [4], ion-selective electrodes [5], separation of superheavy elements [6], and the preparation of contrast agents for magnetic resonance imaging [7] and radiopharmaceuticals [8].

Crown ethers, due to their size selective nature and ability to transport metal ions into non-aqueous media, have also been used effectively as reagents in separation chemistry employing the solvent extraction technique [9, 10]. Recently, crown ethers have been recommended as suitable extracting agents for plutonium due to their specificity as well as high stability to chemical and radiation attack [11], although further work needs to be carried out in this direction. The available reports in the literature on the extraction behaviour of plutonium in the presence of crown ethers are limited only to nitric acid medium and no such data are available for hydrochloric acid medium [12, 13]. The complexation and redox behaviour of plutonium differs significantly in HCl medium as compared to that in HNO_3 [14].

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The present work is the first report on the extraction of Pu(IV) from HCl medium employing nitrobenzene solutions of crown ethers.

2. Experimental

2.1. Reagents

The crown ethers employed in the present work (Figure 1) viz. benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DC18C6), dibenzo-24-crown-8 (DB24C8) and dicyclohexano-24-crown-8 (DCH24C8) were procured from E. Merck (B15C5 and 18C6) as well as Aldrich Chemical Co. Inc. (DB18C6, DC18C6, DB24C8 and DC24C8) and were used without further purification. A.R. grade ammonium metavanadate was obtained from B.D.H. (Bombay) and used as such. Nitrobenzene was obtained from Fluka Chemie AG and was purified prior to use following a literature method [15]. ^{239}Pu was prepared and purified as reported earlier [16].

2.2. Procedure

The effect of crown ether concentration (0.01M–0.05M) on the distribution ratio of plutonium was investigated at 6M HCl for B15C5, DB18C6, 18C6 and DB24C8 and at 3M HCl for DC18C6 and DC24C8. The aqueous acidity in these experiments was chosen in such a way that the D values were in the range 0.01 to 100 to ensure better precision.

Plutonium, in 1M HNO_3 solution, was first adjusted to the +4 state by H_2O_2, followed by its extraction into a 0.5M solution of TTA (thenoyltrifluoroacetone) in toluene. The extracted species containing Pu(IV) was subsequently stripped back into an aqueous solution of 1 : 1 HCl. The oxidation state of plutonium in the HCl solution was maintained at +4 by using ammonium metavanadate. This solution, which now contained predominantly Pu(IV), was employed for the extraction experiments after proper dilution.

The crown ethers employed in the present work have a wide range of partition coefficients (P_L) and proton affinity constants (K_{LH}), defined as:

$$P_L = [L]_o/[L]_a; \quad K_{LH} = [LHCl]_o/[L]_o[H^+]_a[Cl^-]_a.$$

Assuming that the Pu concentration was much smaller than the ligand concentration, the total ligand concentration (L_{total}) and equilibrium ligand concentration in the organic phase (L_o) could be correlated as follows:

$$L_o = \frac{L_{total}}{1 + P_L^{-1} + P_L^{-1}[H^+] + K_{LH}^{-1}}. \tag{1}$$

Since the ligand concentration was varied in the range 0.05M to 0.1M, $[H^+]$ could be approximated to be equal to 3M or 6M depending on the experiment.

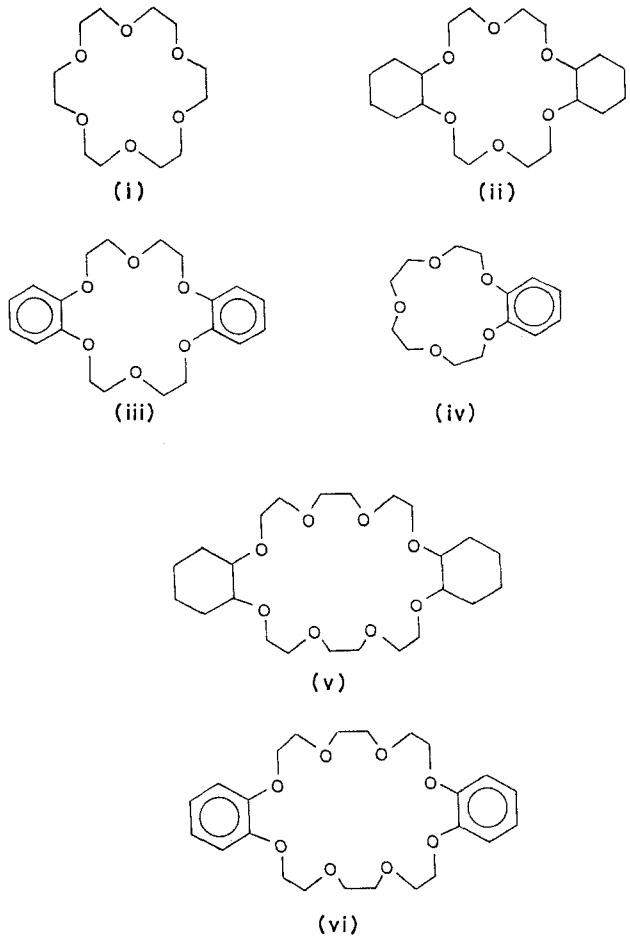

Figure 1. Structures of different crown ethers employed in the present study. (i) 18-crown-6 (18C6); (ii) dicyclohexano-18-crown-6 (DC18C6); (iii) dibenzo-18-crown-6 (DB18C6); (iv) benzo-15-crown-5 (B15C5); (v) dicyclohexano-24-crown-8 (DC24C8); (vi) dibenzo-24-crown-8 (DB24C8).

Thus the terms in the denominator did not vary with ligand concentration and L_o was a constant fraction of L_{total}.

Distribution studies were carried out by equilibrating equal volumes (generally 1 mL) of the two phases (the organic phase contains a suitable concentration of a crown ether in nitrobenzene) for 1 h in a thermostated water bath. ^{239}Pu was assayed subsequently by α-liquid scintillation counting. Nitrobenzene was found to cause significant quenching in the organic phase count rate. Therefore, it was decided to determine the organic phase count rate by taking the difference of the total count rate and the aqueous phase count rate. The validity of this approach was

Table I. Effect of holding oxidants on Pu extraction; [HCl] = 6 M; [DB18C6] = 0.05 M; diluent: nitrobenzene.

Oxidant	Conc.	D		
		30 min.	60 min.	120 min.
$KBrO_3$	2×10^{-4} M	1.88	1.01	0.53
NH_4VO_3	1×10^{-4} M	3.50	2.24	1.48
H_2O_2	2×10^{-4} M	2.18	1.87	1.47
None	–	1.32	0.87	0.43

counterchecked by assaying a few organic phase samples by the gas proportional counting technique. The distribution ratio (D) was defined as

$$D = \frac{\text{Concn. of Pu in the organic phase per unit volume}}{\text{Concn. of Pu in the aqueous phase per unit volume}}$$

Distribution ratio values were measured with a precision of ±5%.

3. Results and Discussion

In experiments involving Pu(IV) in solution, adjustment of the valency state is essential [17]. As the stability of Pu(IV) in the presence of HCl is rather poor, the presence of a holding oxidant in the aqueous phase was mandatory [18]. Table I gives the extraction data of Pu in the presence of different holding oxidants. It was observed that although ammonium metavanadate was the most suitable holding oxidant among those used, there was a tendency for distribution ratio values to decrease with time, suggesting reduction of Pu(IV) to Pu(III).

3.1. Optimization of the Metavanadate Concentration and Equilibration Time

Figure 2 shows the distribution data for Pu as a function of metavanadate concentration as well as the time of equilibration. It was observed that 5.3×10^{-4} M vanadate and 30 min of equilibration time were optimum values for this purpose. Figure 2 also shows that the distribution ratio values attained a maximum of ~16 for the given set of experimental conditions and then decreased continuously to rather low values. Though the exact mechanism of this peculiar behaviour is not understood, it seemed apparent that an optimum concentration of the holding oxidant was required for achieving the maximum D value. In view of the close redox potential values for PuO_2^{2+}/Pu^{4+} and VO_2^{+}/VO^{2+} couples, it was possible that the excess amount of metavanadate ($> 5.3 \times 10^{-4}$ M) led to the formation of a significant concentration of Pu(VI) [19]. Due to the poorer partitioning of the oxygenated extracted species $[PuO_2Cl_4^{2-}]\cdot[HL^{+}]_2$ as compared to that of $PuCl_6^{2-}(HL^{+})_2$, observed D values in

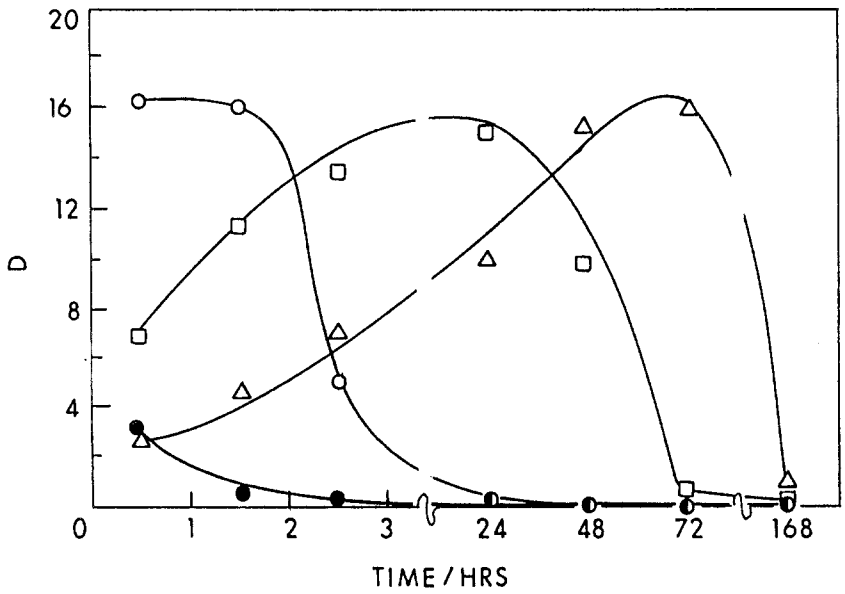

Figure 2. The effect of equilibration on distribution ratio (D) values for various metavanadate concentrations; (●) 5.3×10^{-5} M; (○) 5.3×10^{-4} M; (□) 2.1×10^{-3} M; (△) 5.3×10^{-3}; diluent: nitrobenzene.

the presence of Pu(VI) were lower. With the increase of equilibration time, D values decreased due to the increasing proportion of Pu(III) (formed by the reduction of Pu(IV) by Cl^-), which did not form extractable ion pairs under the experimental conditions chosen.

3.2. Effect of the Organic Diluent

Different organic diluents were used to study their effect on the distribution of Pu(IV) (Table II). It was observed that in spite of the favourable partition of 18C6 [10] towards $CHCl_3$ (6.75) compared to CH_2Cl_2 (4.50) and nitrobenzene (0.1) the extractability was poorer in chloroform, indicating that the solvation of the extractable ion-pair species by the diluents played an important role in the extraction process. Diluents with high dielectric constants, such as nitrobenzene and dichloromethane, showed better extracting ability. The increasing trends in extraction with increasing dielectric constant value of the organic diluent was suggestive of the ion-pair nature of the extraction process. The species extracted were those involving the anionic complexes of plutonium. It was reported earlier [12] that the $D_{Pu(IV)}$ values in the presence of 0.05M DC18C6 in toluene increased with the HNO_3 concentration up to 5 M, followed by a continuous decrease up to 8 M, which was in sharp contrast to the results obtained in the present work showing

Table II. Diluent effect on Pu(IV) extraction using 0.05 M 18C6; [HCl] = 6 M

Diluent	Dielectric constant	%*E*
Dodecane	2.0	1.154
CCl_4	2.23	1.451
Toluene	2.40	2.159
$CHCl_3$	4.81	2.873
CH_2Cl_2	9.08	23.11
Nitrobenzene	35	98.67

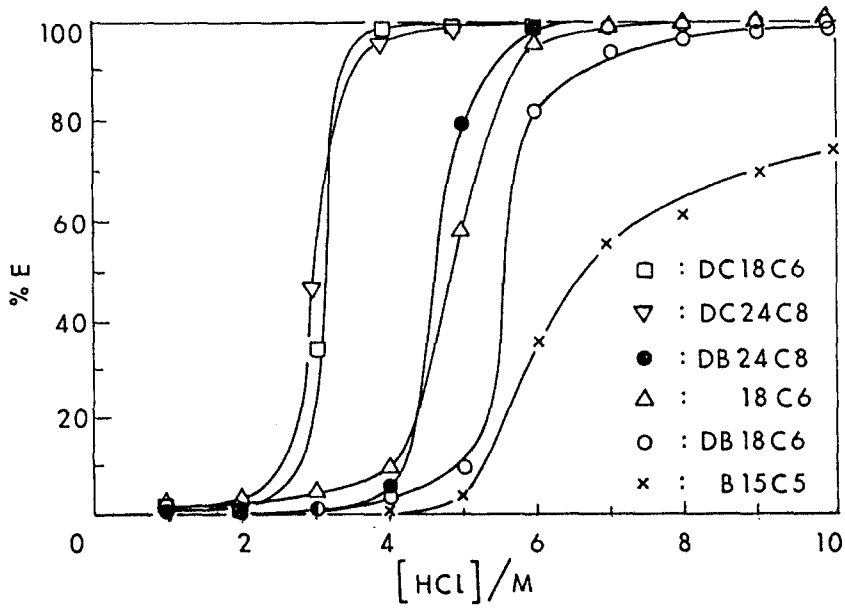

Figure 3. Percentage extraction of plutonium as a function of HCl concentration; [*L*] = 0.05 M; diluent: nitrobenzene.

a continuous increase in *D* values up to 10 M (Figure 3). This further corroborated the extraction of ion-pair species in the present study.

3.3. Effect of HCl Concentration

Figure 3 gives the extracting curves as a function of HCl concentration. It can be seen that the extracting ability of the crown ethers employed in the present work is in the order DC24C8 ~ DC18C6 > DB24C8 ~ 18C6 > DB18C6 ≫ B15C5 employing 0.05 M ligand. Whereas quantitative extraction was observed in the case of DC18C6 and DC24C8 at 5 M HCl, acidity had to be increased to 7 M for DB18C6 and 18C6 and 9 M for DB24C8. It was not possible to extract

Pu quantitatively using 0.05 M B15C5 even up to 10 M HNO_3. There was no correlation of the cavity radii of the ligands with the corresponding D values. The extraction behaviour of Pu(IV) as well as U(VI) in benzonitrile medium from nitric acid solution has been reported earlier [12].

In spite of the large variation in the ionic radii of these two ions, the order of their extractability with ligands of different cavity sizes followed the same trend which is largely similar to that observed in the present work. This suggested that the nature of substituent rather than the size of the crown ether played an important role in the extraction of actinides [19]. As shown in Figure 3, Pu could be stripped quantitatively (>99%) with 1 M HCl for all crown ethers. This behaviour was in sharp contrast to that in nitric acid medium where complexing agents like oxalate, sulphate or reducing agents like hydroxylamine and ascorbic acid were usually employed for quantitative stripping of tetravalent plutonium [12].

3.4. SPECIATION

Plots of log D vs log $[L]_{total}$ suggested extraction of 1 : 2 species for B15C5 and mixed species (Figure 4) of 1 : 1 and 1 : 2 (M : L) stoichiometry for other crown ethers under the experimental conditions employed. It appeared that a combination of species of the types (2) $[HPuCL_6^-]\cdot[HL^+]$ and (3) $[PuCl_6^{2-}]\cdot[HL^+]_2$ were co-extracted into the nitrobenzene phase [20]. The presence of $HPuCl_6^-$ has been reported earlier in strong HCl [21]. In view of the extraction of the species of the type (i) and (ii), the probable extraction equilibria could be represented as:

$$Pu^{4+} + 6Cl^- + L_{(org.)} + 2H^+ \rightleftharpoons [HPuCl_6^{2-}]\cdot[HL^+]_{(org.)} \quad (2)$$

$$Pu^{4+} + 6Cl^- + 2L_{(org.)} + 2H^+ \rightleftharpoons [PuCl_6^{2-}]\cdot[HL^+]_{2(org.)} \quad (3)$$

where L represented the crown ether. Shukla *et al.* [12] have reported the extraction of species of the type $PuL^{4+}(NO_3^-)_4$ from nitric acid medium. However, it was difficult to understand the preference of a large ionic potential cation like Pu^{4+} towards neutral crown ether ligands rather than towards anionic nitrate as suggested by them. It was similarly difficult to comprehend the formation of 1 : 1 (metal : crown ether) species for the large uranyl ion (ionic diameter = 2.8 Å–4.7 Å) [22] and 1 : 2 sandwich complex species for the small Pu(IV) ion (ionic diameter = 1.90 Å) [23] as reported by these authors.

4. Conclusions

Quantitative extraction of Pu(IV) from HCl medium was possible in the presence of crown ethers. There was no correlation of the size of the crown ether cavity with the corresponding D_{Pu} values. Ligands with the cyclohexano substituents were found to be better extractants than those without substituents or with benzo substituents.

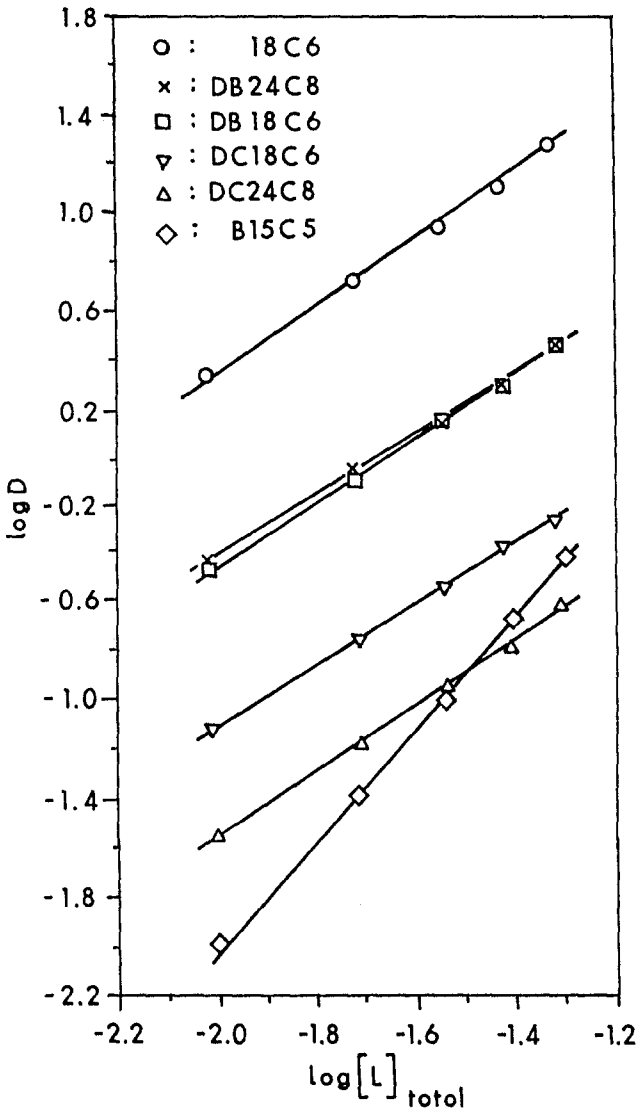

Figure 4. Variation of log *D* with log [L] at 6 M HCl (18C6, DB18C6, B15C5, DB24C8) and 3 M HCl (DC18C6 and DC24C8).

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