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Extraction Studies of Am(III) and Eu(III) with a Tris-Bipyridyl Macrobicyclic Ligand

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Abstract. Complexation of Am(III) with a tris-bipyridine cryptand (L) has been carried out in a non-aqueous medium (CH_3CN—$CHCl_3$). Subsequently the complexation behaviour was investigated using the reverse extraction tracer technique with dinonyl naphthalenesulphonic acid (HD) in toluene as the organic phase and varying concentration of HCl (upto 2M) as the aqueous phase. Equilibrium is attained in the two-phase system at a rate dependent on the hydrogen ion concentration in the aqueous phase. Whereas it takes only a few minutes to attain the equilibrium state at pH 6.0, a phase contact period of 50 days was insufficient if the acidity is greater than 0.4M, presumably due to the slow dissociation of the cryptate formed. The large enhancement in the distribution ratio value in the synergistic system with 1M HCl as the aqueous phase under non-equilibrium conditions is employed for the analytical separation of Am(III) from Eu(III).

Key words: Americium, tris-bipyridine cryptand, extraction, dinonylnaphthalene sulphonic acid.

1. Introduction

Lanthanides form thermodynamically stable and kinetically quite inert complexes with ionizable macrocyclic ligands as compared to those formed with neutral crown ethers and diazacrown ethers [1, 2]. Due to this remarkable property potential applications of these ligands have been envisaged in magnetic resonance imaging [3] as well as for radiolabelling monoclonal antibodies [4]. Macrobicyclic ligands, on the other hand, have been reported to form thermodynamically weaker but kinetically comparable inert complexes in the aqueous medium [5, 6]. Promising results have been obtained on the stabilization of the unusual oxidation states of lanthanides using these ligands. Lehn and co-workers have been investigating the photophysical and structural properties of the complexes of polypyridine ligands with several lanthanides and proposed the use of Eu(III) and Tb(III) cryptates for luminescence immunoassays [7]. They reported that these ligands can efficiently protect the encapsulated lanthanide ion from solvent (water) molecules [8]. The liphophilic nature of the cryptand and the simultaneous decrease in the number of associated water molecules is expected to facilitate the transfer of cations towards the organic phase.

We recently reported that, due to its large hydration energy, Am(III) forms weak outer sphere complexes with crown ethers and diazacrown ethers in the aqueous

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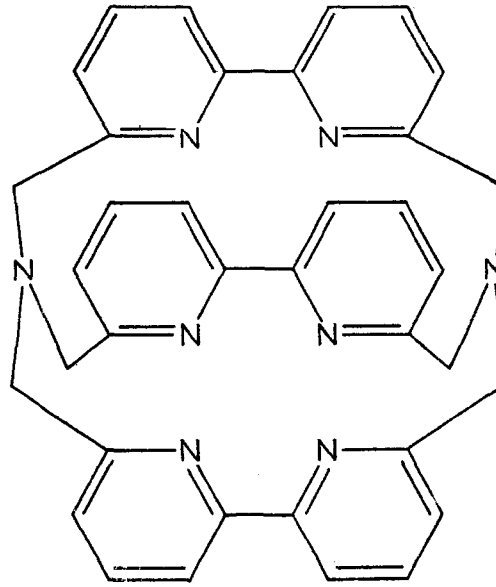

Fig. 1. Tris-bipyridine cryptand (L).

phase [9, 10]. The solvent extraction behaviour of the complexes of lanthanides and actinides employing ionizable macrocyclic ligands has also been investigated and a method has been proposed for the kinetic control of lanthanide selectivities [11, 12]. The present work is the first attempt to investigate the extraction behaviour of Am(III) and Eu(III) using a polypyridine macrobicyclic ligand, L (Figure 1). Apart from preventing the water molecules from interacting with the encapsulated metal ion, pyridine groups may also facilitate the charge transfer from metal to ligand imparting additional covalent character. Therefore it was of particular interest to investigate and compare the complexation of Am(III), an ion with partly filled $5f$-orbitals with Eu(III), an ion with relatively shielded $4f$-orbitals.

2. Experimental

2.1. Materials and Reagents

^{152,154}Eu is prepared by irradiating 'specpure' Eu_2O_3 in a nuclear reactor. ^{241}Am is obtained as a daughter product of ^{241}Pu and was freed from α-emitters and other fission products using a method published by Hall and Herniman [13]. Purity of the tracers is ascertained by alpha and gamma spectrometry. The tris-bipyridine-macrobicyclic ligand in the NaBr form was obtained as a gift from Professor Jean-Marie Lehn. Dinonylnaphthalene sulphonic acid (HD) was procured from R. T. Vanderbilt Co., U.S.A. All the other reagents were of AR grade.

2.2. Distribution Studies

2.2.1. *Forward Equilibrium*

The required amount of tracer in the chloride form is heated to dryness and dissolved in the aqueous phase comprising 1M tetramethyl ammonium chloride adjusted to pH 3.0 or pH 6.0. 1×10^{-3} M $(CH_3)_4ND$ in toluene (prepared by pre-equilibrating HD with 4M tetramethyl ammonium chloride overnight) served as the organic phase.

2.2.2. *Backward Equilibrium*

The complex formation between the metal ion and cryptand is carried out in a 1 : 1 mixture of acetonitrile and chloroform by refluxing at 70°C for 12 h (overheating the mixture resulted in the decomposition of the complex). A similar method was followed by Alpha *et al.* [8] for the synthesis of tris-bipyridine cryptates of lanthanides. Quantitative evaporation of the solvent from the complex is carried out at room temperature. HD of the required concentration in toluene is added to the dried complex. The desired volume of the organic phase (0.5–1.0 mL) was distributed over several extraction tubes followed by its equilibration with 0.5–1.0 mL of the desired aqueous phase (0.2–2.0M HCl).

As mentioned earlier, experiments employing the aqueous phase in the pH range employed $(CH_3)_4ND$ rather than HD as the extractant. It may not be possible to quantitatively correlate the data in the pH range with that obtained in the acidic range due to the lower HD concentration employed in the pH experiment where a micelle extraction mechanism does not operate. In addition, the tetramethylammonium ion used for the ionic strength adjustment has a different selectivity for HD in comparison to the H^+ ion. Due to the small variation in the equilibrium pH compared to the initial pH, use of buffer was found not to be essential. It may, however, be added that the extraction of Am(III) by DNNS has been reported to be independent of pH [16].

The two phases (organic and aqueous) are mixed thoroughly in a thermostated water bath maintained at 25°C and centrifuged just before the withdrawal of suitable aliquots (20–200 μL) for the determination of tracer metal concentrations in these phases by gamma scintillation counting using a NaI(Tl) crystal. The distribution ratio, D, is defined as the ratio of the total metal concentration in the organic phase to that in the aqueous phase.

Experiments involving synthetic mixtures of ^{241}Am and ^{152,154}Eu in the presence of 5×10^{-5} M of L are carried out to determine the separation factor (S.F.) of these two metal ions. Refluxation in the non-aqueous medium (as given above) is carried out for the desired period. An aliquot of the reaction mixture is taken out as and when required and used for the reverse solvent extraction experiments. ^{241}Am and ^{152,154}Eu are determined by monitoring gamma peaks corresponding to 60 keV

TABLE I

Distribution data (D_0) of Am(III) and Eu(III) at different acidities. [HD] = 5×10^{-3} M.

$[HClO_4]$/M	D_0^{Am}	[HCl]/M	D_0^{Am}	D_0^{Eu}
0.2	54.6	0.2	45.0	41.5
0.4	4.56	0.4	4.49	4.23
0.6	1.33	0.6	1.08	1.05
0.8	0.54	0.8	0.40	0.38
1.0	0.28	1.0	0.19	0.18
2.0	–	2.0	0.016	0.019

and 122 keV, respectively. An intrinsic Ge detector (80 CC) supplied by E.G. and G. Ortec coupled to a multichannel analyser was used.

3. Results and Discussion

Trace concentrations of the metal ion (10^{-7} M–10^{-8} M) are helpful in view of the limited availability of the macrobicyclic ligand (10^{-5} M). Though HD is a well investigated, versatile cation exchanger [14, 15], yet it was thought desirable to obtain the distribution data of Am(III) and Eu(III) employing this reagent in a reverse extraction system, predominantly employed in the present work.

3.1. Extraction Behaviour of HD

HD exists in an organic diluent as an aggregate and the aggregation number increases with the decrease of the polarity of the medium [14, 15]. It forms a micelle, thereby facilitating the transfer of the hydrated metal ion from aqueous to the organic phase. The two-phase equilibrium is represented as:

$$M^{3+}(a) + (HD)_n(o) \rightleftharpoons MH_{n-3}D_n(o) + 3H^+(a) \quad (1)$$

where M = Am/Eu; $(HD)_n$ represents the micelle of the extractant, with n being the aggregation number. As expected from Equation (1), the distribution ratio (D_0) varied with [HD] and $[H^+]$ with a dependence of 1 and –3, respectively.

Table I shows the distribution data in HCl and $HClO_4$ media obtained by the reverse extraction technique. The values obtained at 1M HCl and 1M $HClO_4$ are in good agreement with the data reported by Khopkar and Narayankutty [16] on the basis of their forward extraction experiments. Lower D_0 values for HCl compared to those for $HClO_4$ are attributed to the aqueous chloride complexation of Am(III). Table I also shows that the distribution ratio values of Am(III) are very close to the values for Eu(III) in the HCl concentration range 0.2–2.0 M. Separation of the two metal ions under these experimental conditions thus appears quite challenging.

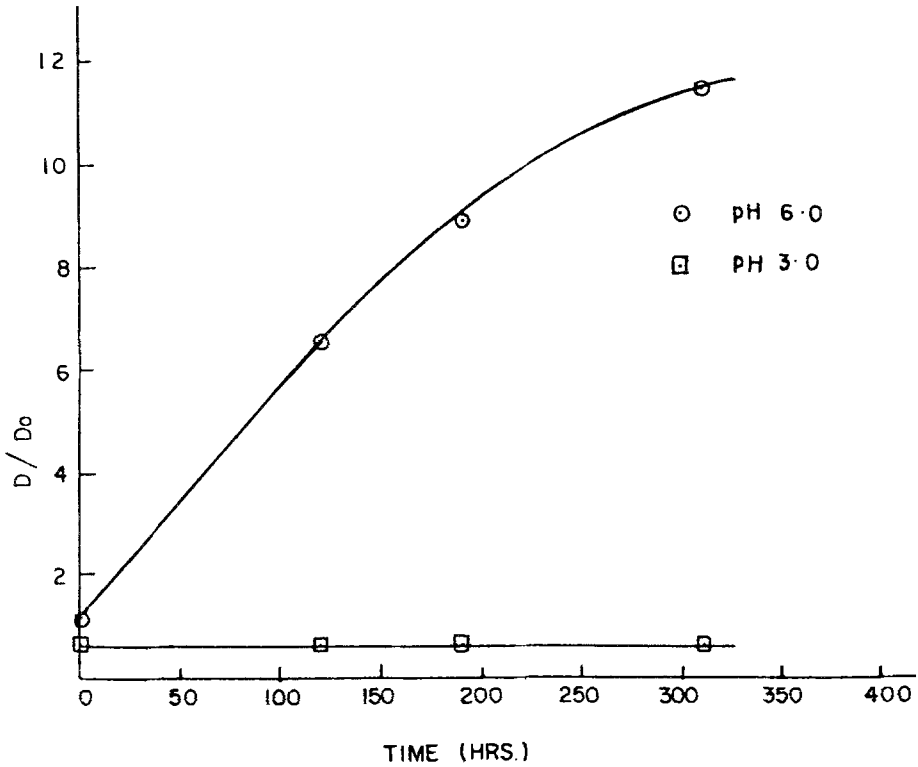

Fig. 2. Variation of D/D_0 with time in forward extraction experiments; $[(CH_3)_4ND] = 0.001M$; $[L] = 7 \times 10^{-5}$ M.

3.2. Distribution Studies in the Presence of L

Figure 2 shows the forward distribution data of Am(III) in the presence of L as a function of time. There is very little change in the D value at pH 3.0 over a two-week period. On the other hand the D value increases significantly at pH 6.0 but the two-phase equilibrium is not attained during this period. The decrease in the D value (with respect to the D_0 value) at pH 3.0 is due to the interaction of DNNS with the protonated form of L, thereby significantly decreasing the effective concentration of the former. At pH 6.0, this decrease is countered by the increased complexation of Am(III) with L and thereby the organophilicity of the metal-bearing species.

In view of the unusually slow kinetics of formation of the complex in the aqueous phase, an alternate scheme is followed in the present work. The complexation reaction is carried out in advance in the non-aqueous medium (CH_3CN—$CHCl_3$) and the cryptate formed is contacted (after complete evaporation of the solvent) with the desired aqueous phase. There is a significant enhancement in the D value in the presence of L, though the extent of enhancement (represented as D/D_0) is influenced by the acidity of the aqueous phase and the period of contact of

the two phases. Figure 3 shows that the equilibrium is reached rather quickly at pH 3.0 as well as at pH 6.0. The relatively larger enhancement at pH 6.0 (4.5 times) compared to the enhancement at pH 3.0 (2.5 times) suggests that the proportion of complexation is influenced strongly by the hydrogen ion concentration. The enhancement in the D value appears to be due to the increased organophilic nature of the cryptate with respect to the uncomplexed hydrated metal ions. Figure 3 also shows the variation of enhancement for the HCl concentration range 0.2–1.0M as a function of time and there is a tendency for the D/D_0 values in each case to approach unity over a period of a few weeks. It is interesting that the enhancement observed is much larger at 1M acidity (14 times) compared to that at 0.2M HCl (2 times) after a contact time of 2 h. This is a direct consequence of the kinetically inert nature of the cryptate formed. The macrobicyclic complex, originally present in the organic phase, has to undergo dissociation several times, more at 1M $[H^+]$ compared to that at the lower acidities, to attain blank distribution values (D_0).

Figure 4 shows that whereas, in the absence of L, the expected slope of approximately 3 is obtained for the straight line plot of log D vs. log a_{H^+} in the acidity range 0.2–1.0M, in the presence of L, there is no linear correlation of log D with log a_{H^+}. This is again due to the fact that whereas D values in the absence of L refer to the equilibrium states, those in the presence of L do not refer to the state of equilibrium. Figure 4 shows that after 1272 h. when D for 0.2M HCl has already dropped to the corresponding D_0 value, in other cases they progressively deviate from their corresponding D_0 values. Table II shows that the decrease in the D values of Am(III) in the synergistic system depends on the hydrogen ion concentration.

On the basis of their crystal structural work, Walksman *et al.* [17] have recently reported the presence of Cl^- ion in the Eu(III)-cryptate. Accordingly the existence of species of the type $AmLCl^{2+}$ along with AmL^{3+} cannot be ruled out in the present work. However, the co-extraction of such species towards the organic phase with cation exchanger HD may not be significant.

The experiments carried out with 18-crown-6, 1,10-diaza-18-crown-6 or 2,2′-bipyridyl ligand in place of L showed no enhancement in the D values if 1M HCl is chosen as the aqueous phase. This is explained on the basis of the relatively weaker interaction of these ligands with metal ions and consequently the faster dissociation kinetics. We have recently reported such weak outer sphere complexation of Am(III) with crown ethers in the aqueous phase [9]. This is in sharp contrast to the strong complex formation of lanthanides with cryptands reported by Burns and Baes [5].

There is no reference available in the literature on the extraction behaviour of trivalent actinide ions in the presence of the cryptands. Ensor *et al.* [18] have reported the forward extraction behaviour of several lanthanides in the presence of tert-butyl-15-crown-5 at pH 2.0. Equilibrium is attained in their system relatively faster (within 6 h.), though the enhancement is also much smaller. These observations are in conformity with the weak outer sphere nature of the complexes of

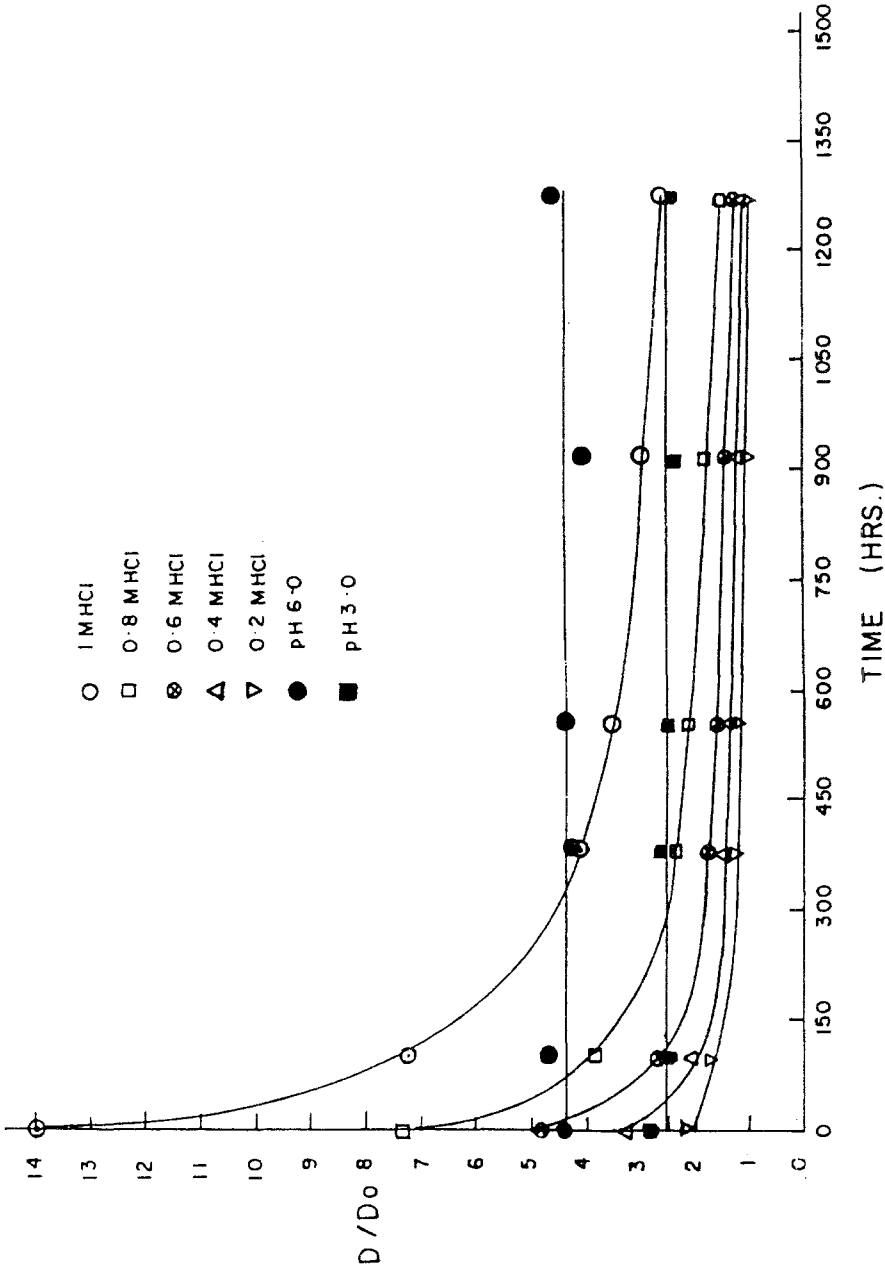

Fig. 3. Variation of D/D_0 with time in reverse extraction experiments; [L] = 5×10^{-5} M; [HD] = 0.005M ([H^+] = 0.2–1.0M); [$(CH_3)_4ND$] = 0.001M (pH = 3.0 and pH = 6.0).

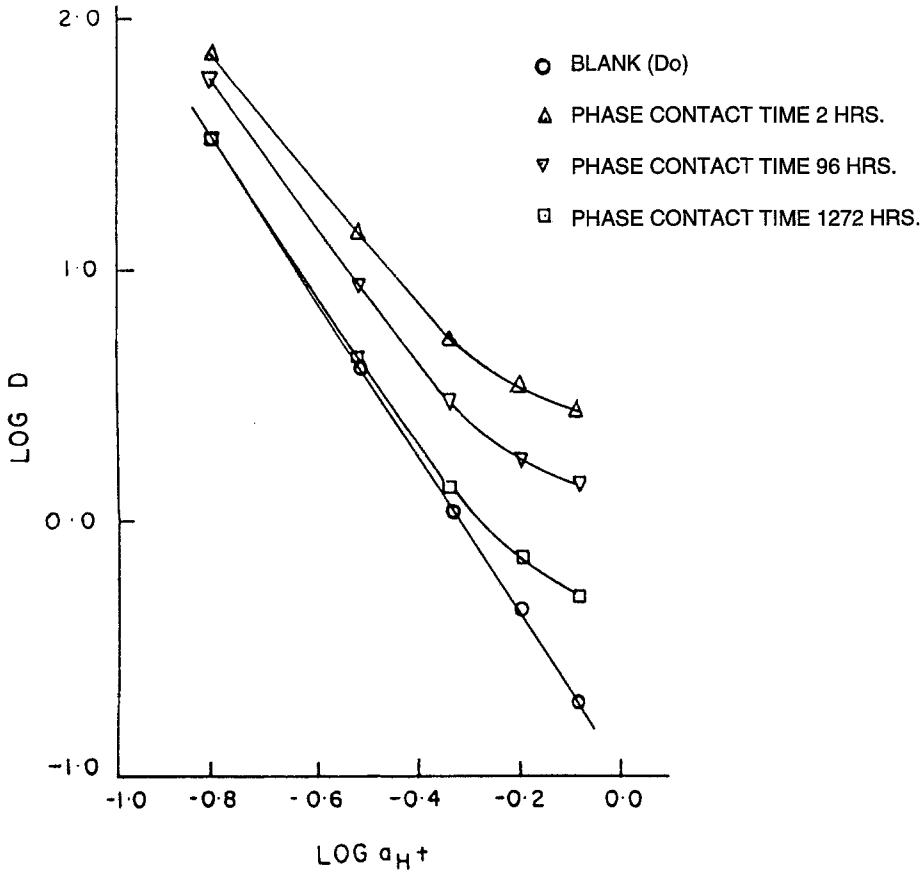

Fig. 4. Variation of log D with log a_{H^+}; [HD] = 0.005M; [L] = 5×10^{-5} M.

TABLE II

Decrease in D value of Am(III) in the synergistic system as a function of acidity; [L] = 5×10^{-5} M; [HD] = 5×10^{-3} M.

$[H^+]$	D_2	D_{1272}	D_2/D_{1272}
1.0	2.64	0.49	5.4
0.8	3.28	0.69	4.8
0.6	5.11	1.32	3.5
0.4	13.38	4.35	3.1
0.2	71.21	32.23	2.2

Note: The subscripts of D refer to the phase contact time in hours.

trivalent metal ions with crown ethers as demonstrated by Rogers *et al.* [19].

Due to the difference in the reactivity of electrons in the $4f$ and $5f$ orbitals

TABLE III

Distribution data of Am(III)/Eu(III) as a function of refluxation time; [HD] = 5×10^{-3} M; [HCl] = 1.0M; phase contact time = 2 h; [L] = 5×10^{-5} M.

	D		
Time (h)	Am(III)	Eu(III)	S.F.
0.5	1.16	0.54	2.32
2.0	1.93	0.85	2.27
6.0	2.38	1.28	1.86
12.0	3.36	1.40	2.40

towards the pyridyl groups, Eu(III) and Am(III) interact with L to varying degrees. In addition, the crystal ionic radius for co-ordination number 8 of Eu(III), 1.206 Å, is also somewhat smaller than that of Am(III) (1.230 Å) [20]. The cavity radius of the ligand (as an analogy to cryptand 2.2.2) is close to 1.4 Å[21], implying better size compatability with Am(III). Both these factors are likely to favour the complexation and thereby the extraction of Am(III) over Eu(III). A synthetic mixture of ^{241}Am and ^{152,154}Eu is employed in the reverse extraction experiments to obtain the separation factor of these two elements in the presence of L. Table III shows the distribution data as a function of refluxation time for the two cations. The average separation factor of 2.2 ± 0.2 is distinctly larger than the corresponding value in the absence of L (1.1 ± 0.1).

4. Conclusions

The distribution studies on Am(III)/Eu(III) tris-bipyridine cryptate have revealed acid-assisted, slow dissociation of the complex. It has been found to be possible, on the basis of the reverse extraction technique, to devise an improved separation procedure of Am(III) over Eu(III) under non-equilibrium conditions. It would be of particular interest to explore the effect of phase contact time (in the range of seconds) on the separation factors for the metal ions with varying degree of complexation. Employment of longer equilibration periods may result in quantitative dissociation of the cryptate formed and consequently poorer separation factors.

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