

Room temperature ionic liquid diluent for the extraction of Eu(III) using TRUEX extractants

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Abstract Extraction of europium(III) from nitric acid medium by a solution of tri-*n*-butylphosphate (TBP) and *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in the room temperature ionic liquid, 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (amimNTf₂ where a = butyl or hexyl or octyl), was studied. The distribution ratio of ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) in TBP-CMPO/bmimNTf₂ was measured as a function of various parameters such as the concentrations of nitric acid, CMPO and NaNO₃. Remarkably large distribution ratios were observed for the extraction of europium(III) when bmimNTf₂ acted as diluent. The stoichiometry of metal-solvate in organic phase was determined by the slope analysis of extraction data.

Keywords Europium · Americium · *n*-Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide · tri-*n*-Butylphosphate · Room temperature ionic liquid · Distribution ratio

Introduction

Room temperature ionic liquids (RTILs) are the organic salts molten at temperatures lower than 100 °C [1]. RTILs are receiving increased attention for possible applications in the area of nuclear fuel cycle. The properties such as

insignificant vapour pressure, amazing ability to dissolve organic and inorganic compounds, tuning to task-specific form etc. make the RTILs popular for reprocessing applications [2, 3]. RTILs were explored as diluents for nuclear fuel cycle applications since the last decade [4–8]. The results obtained from those studies indicated that the extractants in conjunction with RTIL diluents have provided an unprecedented extraction of target metals from aqueous solution under the condition that gave negligible or meager extraction with customary diluents. This was attributed to the extraordinary solvating ability of RTILs in the extracted phase. Dietz and co-workers [5, 6] studied the extraction behavior of several metal ions of nuclear interest by appropriate neutral extractants present in RTIL medium. Ion exchange between target metal ion and RTIL was reported as one of the prevalent mode of metal transfer in RTIL phase.

After the separation of uranium and plutonium in the PUREX process, the concentrated raffinate is known as high-level liquid waste, which contains significant quantities of trivalent actinides (An(III)) and lanthanides (Ln(III)). These are generally partitioned by a solution of 1.2 M tri-*n*-butyl phosphate-0.2 M *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in *n*-dodecane [9–11]. In this context, Nakasima et al. [12] reported the distribution ratio of lanthanides by CMPO/RTIL at various nitric acid concentrations. However the detailed extraction behavior of europium(III) in the solution of CMPO–TBP in RTIL was not reported so far. Therefore, the objective of the present paper is to report the results of the studies on the extraction of europium(III) by CMPO–TBP present in ionic liquid medium namely 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (alkyl = butyl, hexyl, octyl) and to compare the results with that of the conventional TRUEX solution. The distribution ratio of ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) in

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CMPO–TBP-/bmimNTf₂ was measured as a function of various parameters such as concentrations of nitric acid, CMPO, NaNO₃ and the nature of diluent .

Experimental

Materials

All the chemicals and reagents used in this study were of analytical grade. 1-methylimidazole and 1-chlorobutane were procured from Lancaster, UK. 1-methylimidazole was distilled before use and other chemicals were used without any purification. Tri-*n*-butylphosphate was obtained from E. Merck, Mumbai. Bis(trifluoromethanesulphonyl)imide lithium salt (Li(NSO₂CF₃)₂; NTf₂ = (NSO₂CF₃)₂) was procured from Fluka.

Preparation of amimNTf₂

The procedure adopted for the synthesis of amimNTf₂ (i.e., bmimNTf₂, hmimNTf₂, omimNTf₂) has been described elsewhere [1]. Yield of ionic liquids were ~85%. Viscosity of bmimNTf₂, hmimNTf₂ and omimNTf₂ were 36 cP, 50cP and 62 cP respectively at 298 K. IR spectra indicated the following bands, 3175, 3122 cm⁻¹ (C–H stretch) imidazole ring, 2964, 2932, 2868 cm⁻¹ (C–H stretch) aliphatic, 1564, 1465, 1168 cm⁻¹ imidazole ring symmetric stretch, 1425, 1378 (MeC–H asymmetric stretch), 1138 cm⁻¹ (SO₂ symmetric stretch).

Effect of [HNO₃]

All equilibration experiments were conducted in duplicate at 303 K with 1:1 aqueous to organic phase ratio. The experiments involved equilibration of aqueous and organic phases (1 mL each) present in a 10 mL capacity test tube immersed in a constant temperature water bath and rotated in up-side-down manner for about 3 h. However, it was found from the rate of extraction studies that equilibrium was established in 30 min. Tri-*n*-butyl phosphate solution in amimNTf₂ and TBP-CMPO in amimNTf₂ (or *n*-DD) were prepared. The concentration of CMPO was varied depending upon the type of experiment. The organic phase was pre-equilibrated with desired concentration of nitric acid. Extraction of europium(III) as a function of nitric acid concentration was studied by equilibrating 1 mL of organic phase with 1 mL of nitric acid solution containing ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) tracer (20 mg/L). The concentration of nitric acid in the test solution was varied from 1 to 5 M. After three hour of equilibration, the radioactivity of ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) distributed between organic and aqueous phases was measured using a well-type NaI(Tl) scintillation detector. The distribution ratio (D_{Eu}) of europium was determined by using Eq. 1. Similar experiment was also performed with *n*-DD diluent.

$$D_{Eu} = \frac{[{}^{(152+154)}Eu]_{org}}{[{}^{(152+154)}Eu]_{aq}} \quad (1)$$

For comparing the extraction trend of ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) with ²⁴¹Am(III) (20 mg/L), the distribution ratio of ²⁴¹Am(III) was also measured both in ionic liquid and *n*-DD diluent in a similar manner. Initially, for comparing the extraction of Eu(III) and Am(III) in ionic liquid with those observed in TRUEX solvent (0.2 M CMPO–1.2 M TBP/*n*-DD), a solution of 0.2 M CMPO–1.2 M TBP in RTIL was used as solvent medium. Later it was found [4] that it was desirable to use 0.05 M CMPO only when ionic liquid acted as diluent as the distribution ratio obtained in this case were comparable with *n*-DD solution (i.e. TRUEX solvent).

Effect of [CMPO]

Extraction of europium as a function of CMPO concentration in the ionic liquid phase was studied by equilibrating the organic phase and desired concentration of nitric acid solution (1–5 M) spiked with ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) tracer. The CMPO concentration in organic phase (CMPO–1.2 M TBP/amimNTf₂) was varied from 0.02 to 0.2 M. The radioactivity of europium after equilibration was measured and distribution ratio was determined using Eq. 1.

Effect of [Eu(III)] in aqueous phase

The effect of europium(III) concentration in aqueous phase was studied by equilibrating the organic phase with a solution of Eu(III) nitrate in nitric acid (1–5 M) spiked with ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) tracer. The concentration of Eu(III) in aqueous phase was varied from 20 to 100 mg/mL. The loading of europium in organic phase was determined by measuring the radioactivity of organic and aqueous phases.

Effect of [NO₃⁻]

The concentration of nitrate in the aqueous phase was varied by diluting the desired quantity of NaNO₃ solution (concentrated stock) in HNO₃. This aqueous phase was equilibrated with organic phase (0.05 M CMPO–1.2 M TBP/bmimNTf₂) spiked with ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) and the distribution ratio was determined as described above.

Results and discussion

Effect of nitric acid

The distribution ratio of europium(III) in 0.2 M CMPO–1.2 M TBP/bmimNTf₂ at various concentrations of nitric acid at 303 K is tabulated in Table 1. The data are

Table 1 Distribution ratio and separation factor (SF) of americium(III) over europium(III) achieved by using 0.2 M CMPO–1.2 M TBP in bmimNTf₂ (or *n*-DD) as a function of nitric acid

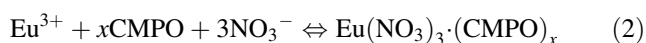
[HNO ₃] _{aq} /M	Distribution ratio in 0.2 M CMPO–1.2 M TBP/bmimNTf ₂		Distribution ratio in 0.2 M CMPO–1.2 M TBP/ <i>n</i> -DD		SF = D _{Am} /D _{Eu} in	
	⁽¹⁵²⁺¹⁵⁴⁾ Eu(III)	²⁴¹ Am(III)	⁽¹⁵²⁺¹⁵⁴⁾ Eu(III)	²⁴¹ Am(III)	bmimNTf ₂	<i>n</i> -DD
1	1040	1975	8.8	12.5	1.9	1.4
2	560	810	11.7	14	1.45	1.2
3	408	520	13	17	1.44	1.3
4	240	282	11	14.5	1.17	1.3
5	160	188	10.5	13	1.17	1.2

T = 303 K

compared with the distribution ratio of europium(III) in *n*-dodecane (*n*-DD) system as well as with Am(III) under similar conditions. Extraction of ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) in 1.2 M TBP/bmimNTf₂ was determined to be insignificant and it was of the order of $\sim 10^{-2}$. However, remarkable enhancement in the distribution ratio is observed in the presence CMPO as shown in Table 1. The *D* values of ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) in 0.2 M CMPO–1.2 M TBP/bmimNTf₂ decrease from 1040 to 160 with increase in the concentration of nitric acid from 1.0 to 5.0 M. In contrast, a maximum *D* value of ~ 15 is obtained for the extraction of europium(III) and americium(III) in *n*-DD system. This could be attributed to the extraordinary solvating capability of ionic liquid in organic phase, which seems to facilitate the mass transfer of metal ions. Table 1 also shows the comparison of the separation factor (SF = D_{Am}/D_{Eu}), achieved with the use of ionic liquid and *n*-DD diluent. It is observed that the SF are similar in both cases even though the distribution ratio achieved in case of ionic liquid diluent is much higher. Moreover, the *D* value decreases with increase in the concentration of nitric acid and the separation factor also decreases with increase in nitric acid concentration from 1 to 5 M.

Effect of [CMPO]

Several authors [9–11] reported the metal-solvate stoichiometry of various metal ions by slope analysis of the extraction data. The stoichiometry of trivalent actinides and lanthanides in CMPO/*n*-DD system was reported [10, 11] as 1:3. In RTIL diluent, Nakasima et al. have reported the stoichiometry of 1:3 for Ln–CMPO complex [12]. We also studied the metal-solvate stoichiometry of Am(III) in CMPO–TBP/bmimNTf₂ and reported the variation of slope from 3.0 at 1 M nitric acid to 2.1 at 5 M nitric acid [4].



CMPO being a neutral ligand, extracts europium(III) in the form of neutral europium(III) nitrate as shown in Eq. 2. Figure 1 shows the plot of log *D*_{Eu} against log [CMPO]. It

is seen that *D*_{Eu} value increases with increase in the concentration of CMPO. A slope value of 3.0 is obtained for the extraction of europium(III) from 1.0 M nitric acid medium. Thus, the metal-solvate stoichiometry for the extraction of europium(III) by CMPO–TBP/bmimNTf₂ resembles that of TRUEX system at 1.0 M nitric acid medium, wherein three molecules of CMPO are involved in co-ordination with europium in organic phase. A similar 1:3 complex (Ln³⁺:CMPO) was reported for the extraction of some trivalent lanthanides from neutral solution by CMPO/RTIL [12]. In 3.0 M nitric acid medium, the slope decreases to 2.8 (~ 3) and at 5.0 M nitric acid medium the value decreases to 2. A similar observations was noticed in the extraction of Am(III) in CMPO–TBP/bmimNTf₂ [4], indicating more studies are needed to understand the extraction behavior of trivalents (Ln(III) and An(III)) in ionic liquid diluent.

Effect of Eu(III) loading

The effect of europium loading in the aqueous phase on the extraction is shown in the Table 2. The europium concentration in aqueous phase was varied from 20 to 100 mg/mL. Interestingly it is observed that there is no third phase formation even at the maximum europium(III) loading i.e., 100 mg/mL. In conventional *n*-DD system, the limiting organic concentration (LOC) of europium in organic phase was 9 mg/mL and the equilibrium aqueous concentration was 6 mg/mL. However, the present study indicates that by using ionic liquid diluent, bmimNTf₂, the undesirable third phase formation can be easily avoided. More detailed studied are published elsewhere [8].

Effect of diluents

The extraction of ⁽¹⁵²⁺¹⁵⁴⁾Eu(III) in CMPO–TBP in amimNTf₂ (*a* = alkyl (butyl, hexyl and octyl)) as a function of nitric acid concentration was studied and the results are shown in Fig. 2. It is observed that the distribution ratio of

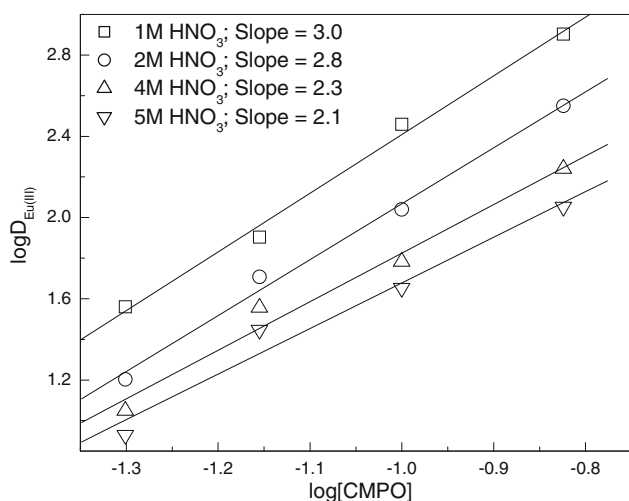


Fig. 1 $\log D - \log[\text{CMPO}]$ plot for the extraction of Eu(III) at 303 K. O:A = 1:1, Equilibration time = 3 h

Table 2 Variation of europium(III) loading in 0.2 M CMPO–1.2 M TBP/bmimNTf₂ at different initial concentrations

[Eu(III)] _{ini} , mg/mL	Organic loading (mg/mL) at different equilibrium acidities [8]		
	1 M	3 M	5 M
20	12.1	12.2	12.4
50	16.0	16.1	15.7
100	22.7	24.2	21.0

$T = 303 \text{ K}$. $[\text{HNO}_3]_{\text{eq}}$, varied [8]

$(^{152+154}\text{Eu(III)})$ decreases with increase in the chain length of alkyl group attached to the cation part of the ionic liquid. This observation is not new to ionic liquid systems. Chun et al. [7] and Dietz et al. [5, 6] have reported the decrease in distribution ratio with increase in the hydrophobicity (due to increase in alkyl chain length) of ionic liquids. This was attributed to the decrease in the ability of ionic liquids to undergo ion exchange with increase of hydrophobicity. However the correct reason for the decrease in distribution ratio observed in the present study is not clear and more studies are needed to understand this behavior.

Effect of $[\text{NO}_3^-]$

The effect of nitrate ion concentration on the extraction of Eu(III) in 0.05 M CMPO–1.2 M TBP/bmimNTf₂ is displayed in the Table 3. It is noticed that the variation in the distribution ratio is insignificant irrespective of the concentration of NO_3^- ion in the aqueous phase. Thus it can be

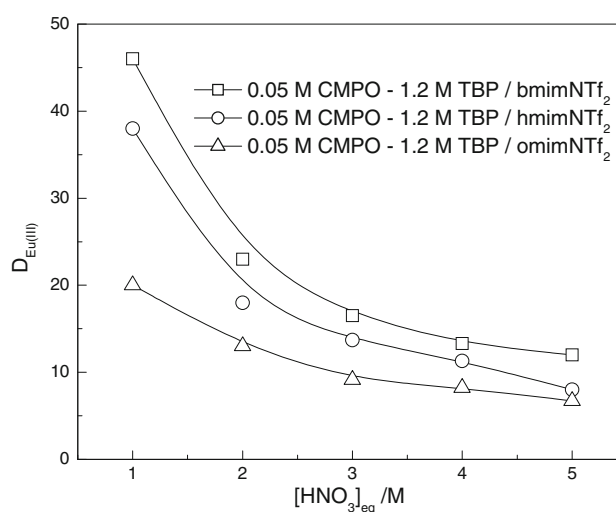


Fig. 2 Distribution ratio of $(^{152+154}\text{Eu(III)})$ in 0.05 M CMPO–1.2 M TBP/bmimNTf₂ (or hmimNTf₂ or omimNTf₂). O:A = 1:1, $T = 303 \text{ K}$

Table 3 Effect of nitrate ion concentration on the distribution ratio of $(^{152+154}\text{Eu(III)})$

[NO ₃ ⁻], M	Distribution ratio of Eu(III) in 0.05 M CMPO–1.2 M TBP/bmimNTf ₂	
	3 M	4 M
0	16.5	13
0.5	15.8	12.8
1	16.6	12.6
1.5	16	12.4

Organic phase = 0.05 M CMPO–1.2 M TBP/bmimNTf₂, Aqueous phase = 3 M HNO_3 + varied NO_3^- concentration, O:A = 1, $T = 303 \text{ K}$

concluded that the salting out effect by NaNO_3 is insignificant.

Conclusions

Remarkable extraction of europium(III) was achieved with the use of ionic liquid diluent. The extraction stoichiometry of Eu(III)–CMPO solvate was 1:3 at 1 M nitric acid and decreased to 1:2 at 5 M nitric acid. Increasing the chain length of alkyl group attached to imidazolium ring decreased the distribution ratio of Eu(III). No third phase formation was observed up to the loading of 25 mg/mL in organic phase.

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