

Solvent extraction studies of plutonium(IV) and americium(III) in room temperature ionic liquid (RTIL) by di-2-ethyl hexyl phosphoric acid (HDEHP) as extractant

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Abstract Solvent extraction of Pu(IV) and Am(III) from aqueous nitric acid into room temperature ionic liquid (RTIL) by an acidic extractant HDEHP (di-2-ethyl hexyl phosphoric acid) was carried out. The D values indicated substantial extraction for Pu(IV) and poor extraction for Am(III) at 1M aqueous nitric acid concentration. However at lower aqueous nitric acid concentrations (pH 3), the Am(III) extraction was found to be quantitative. The least squares analysis of the extraction data for both the actinides ascertained the stoichiometry of the extracted species in the RTIL phase for Pu(IV) and Am(III) as $[\text{PuH}(\text{DEHP})_2]^{3+}$, $\text{AmH}(\text{DEHP})^{2+}$. From the D values at two temperatures, the thermodynamic parameters of the extraction reaction for Pu(IV) was calculated.

Keywords Solvent extraction · Pu(IV) · HDEHP · Room temperature ionic liquid · Thermodynamics

Introduction

Room temperature ionic liquids (RTIL) are important green solvents due to their non volatility, low vapor pressure as well as affinity for both organic and inorganic species. Here green solvent refers to solvents that are non toxic to living things and the environment. Apart from different areas like synthetic chemistry electrochemistry etc., RTILs find applications in the field of separation chemistry also [1–22]. Based on the water miscibility, room temperature ionic liquids are classified as

hydrophilic, hydrophobic and amphiphilic. In this hydrophobic ionic liquids are being projected as possible replacement of volatile organic solvents for the liquid–liquid extraction of metal ions especially heavy metals, lanthanides and actinides by water/RTIL system [3–5]. This was due to their favorable ionic nature and redox stability over conventional organic solvents. The substituted ionic liquids called task specific ionic liquids (TSILs) also finds important applications for metal ion separations [6–8]. Few studies were reported in the literature on the radiation damage of ionic liquids during the extraction of radioactive metal ions [9, 10]. Studies were reported in the literature to understand the influence of cations as well as anions of RTIL, on their physical properties like viscosity, density as well as surface tension [11]. Reports published in the literature indicated that surface active properties of various ionic liquids [12] were important for understanding the micelle formation of ionic liquids, which in turn could influence the third phase formation during liquid–liquid extraction. It has to be emphasized that the main drawbacks of RTILs as solvents for liquid liquid extraction, are their higher viscosity and lower solvating power of metal solute complex at higher metal loading [13]. It is worth mentioning here that for adapting RTILs as solvents for process applications, fundamental data on the extraction behavior are necessary. In this connection, we have previously carried out solvent extraction studies of Pu(IV) by using PF_6^- based RTILs in combination with two complexing agents viz. CMPO, DC18C6 crown ether [17, 18]. The present study is a part of our continuing effort in this direction and was carried out by employing $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anion based ionic liquid which has better stability towards higher aqueous acidities as well as solubility for actinides complexes. With this background, we have taken up the extraction studies of actinides especially Pu(IV) and

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Am(III) by employing HDEHP as the complexing agent in three different $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ based RTILs namely *N*-butyl-3-methyl pyridinium bis (trifluoromethyl sulphonyl) imide (BMPIM), 1,2 dimethyl-3-propylimidazolium- bis (trifluoromethyl sulphonyl) imide (DMPIIM) and 1-hexyl-3-methylimidazolium bis (trifluoromethyl sulphonyl)imide (HMIIM).

Experimental

All the chemicals used were of reagent grade. HDEHP used in the present studies was obtained from E.Merck, Germany. All the RTILs were obtained from io-littec, GmbH, Germany. Pu-239, Am-241 were used as tracers for the extraction studies and the radiochemical purities of both were ascertained by alpha spectrometry.

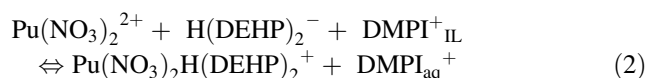
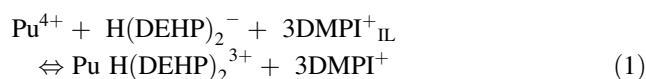
Equal volumes of HDEHP solution in respective RTIL and aqueous solution of required molarity containing Pu(IV) or Am(III) were vortexed for 10 min and were equilibrated in a temperature controlled shaker bath for 30 min. The solution was allowed to stand for phase separation after centrifuging. From this, both the phases were withdrawn for alpha scintillation counting. From the organic and the aqueous phase activity, the distribution ratio (*D*) was calculated.

All the measurements were done in duplicate and *D* values obtained were within $\pm 2\%$, with good material balance (95 %). The back extraction studies were carried out with different strippants mentioned in the text.

Results and discussion

The results obtained by taking three RTILs namely BMPIM, DMPIIM, HMIIM and employing HDEHP for the extraction of Pu(IV) from 1M HNO_3 are shown in Table 1. From the results it can be understood that near quantitative extraction of Pu(IV) is possible at sufficiently high extractant concentrations in all three extraction systems. It was also seen that pyridinium based RTIL (BMPIM) gave better extraction than the other two imidazolium based RTILs (DMPIIM, HMIIM). Even though all the RTILs used are quite stable on contact with higher $[\text{HNO}_3]$, in the present studies, we used 1M nitric acid as the aqueous medium for comparison purpose. The effect of variation of [HDEHP] in different RTILs on the extraction of Pu(IV) from 1M nitric acid was carried out and *D* values were plotted against [HDEHP] in a log–log scale (Figs. 1, 2).

From the slopes of the graphs, it was inferred that 1 molecule of HDEHP takes part in the extraction reaction. It was also indicated that the extraction mechanism of Pu(IV) by HDEHP in RTIL was cation exchange similar to other diluent systems, the difference being the role played by RTIL cation in the extraction reaction. Studies reported in the literature indicated that the mechanism of metal extraction in RTIL could be through anion exchange, cation exchange or solvation, irrespective of the extractants used. Most of the references mentioned in this paper pertaining to solvent extraction of metal ions in RTIL suggested that for neutral donors the mechanism of metal extraction was through cation exchange contrary adduct formation in other organic diluents. However for acidic extractants majority of the studies indicated that the extraction mechanism was through cation exchange similar to that in volatile organic diluents. Studies were also reported in the literature which suggested anion exchange mechanism for the extraction of La(III) with HTTA in RTIL [19]. The effect of $[\text{NO}_3^-]$ on the extraction of Pu(IV) by HDEHP was also investigated by carrying out the extraction from perchloric acid medium by increasing the $[\text{NO}_3^-]$ by adding nitrate salt. The linear increase in *D* values with a slope of around 2 indicated (Fig. 3) the role of NO_3^- ion on the extraction and the stoichiometry of the Pu(IV) complex in RTIL phase can be assumed as $[\text{Pu}(\text{NO}_3)_2\text{H}(\text{DEHP})_2]^{+1}$. The role of NO_3^- on the extraction of Pu(IV) from higher aqueous nitric acid concentrations by HDEHP in volatile organic compounds (VOC) was reported in the literature [23, 24]. It was inferred that the overall extraction reaction was through cation exchange process as given below.



Reaction (1) is expected at very low aqueous nitric acid concentrations. The extraction reaction (2) was inferred from our present studies including nitrate ion variation experiments. Dimerisation of HDEHP was reported in a conventional diluent [25] as well as in RTIL [26] and we have assumed the same thing in our present studies. Even though it was assumed the dimerisation of HDEHP in the bulk, slope analysis indicated that only one HDEHP molecule takes part in the extraction reaction. It can be seen that in both the models explained above, the apparent equilibrium constant (*K*) remains the same and can be calculated as

Table 1 Extraction of Pu(IV) from 1M Nitric acid by HDEHP/RTIL

RTIL	Temp (C)	[HDEHP] M	D
BMPIM	25	0.013	20.5 ± 1.0
	25	0.025	35.4 ± 1.5
	25	0.050	69 ± 1.5
DMPIIM	21	0.001	1.47 ± 0.3
	21	0.007	10.3 ± 0.5
	21	0.013	19.12 ± 1.0
DMPIIM	25	0.001	0.65 ± 0.2
	25	0.007	4.6 ± 0.7
	25	0.013	8.5 ± 0.5
	25	0.025	16.2 ± 1.1
HMIIM	21	0.012	7.2 ± 0.5
	21	0.024	14.6 ± 0.8
	21	0.052	25.2 ± 1.2

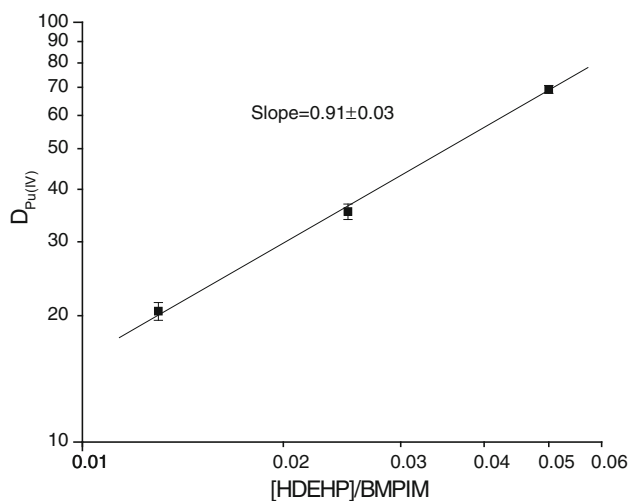


Fig. 1 Log-log plot of *D* versus [HDEHP]/BMPIM

$$K = \frac{[Pu\ H(DEHP)_2^{3+}][DMPI^+]^3}{[Pu^{4+}][H(DEHP)_2^-][DMPI^+]^3} = D/[H(DEHP)_2^-]$$

By knowing the *D* ratios at two temperatures (21°, 25 °C) the *K* values for the extraction of Pu(IV) by HDEHP/DMPIIM were determined. The *D* value due to RTIL alone (*D*₀) was not considered for the calculation of *K* value since it was negligibly small (~0.1). It was found that the *D* value decreases with increase in temperature suggesting that the extraction reaction is exothermic in nature Table 2. The enthalpy change (ΔH) associated with the extraction reaction was found out by using the Van't Hoffs equation,

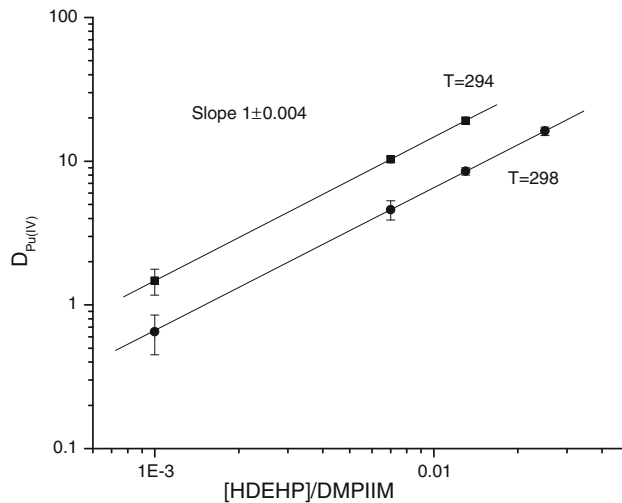


Fig. 2 Log-log plot of *D* versus [HDEHP]/DMPIIM at 294, 298 K

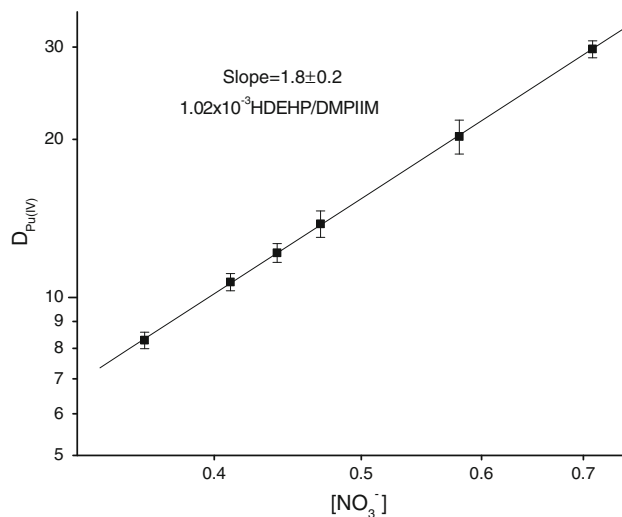


Fig. 3 Log-log plot of *D* versus [NO₃]

Table 2 Thermodynamic data on the extraction of Pu(IV) by HDEHP/DMPIIM

Extractant	log <i>K</i> (298 K)	ΔG (K J/mol)	ΔH (K J/mol)	ΔS (J/mol°)
HDEHP/DMPIIM	2.815 ± 0.002	-16.12 ± 0.01	-148.82 ± 0.42	-445 ± 11

$$\log K_1/K_2 = \Delta H / 2.303R [1/T_2 - 1/T_1].$$

The standard free energy change (ΔG°) is related to the equilibrium constant *K* by the equation

$$\Delta G = -2.303 RT \log K.$$

Table 3 Back extraction studies of Pu(IV) from HDEHP/DMPIIM

Stripping reagent	<i>D</i>	% stripping
3N HCl	0.199	16.6
4N HNO ₃	0.072	6.7
6N HNO ₃	0.038	3.7
1M H ₂ C ₂ O ₄	16.42	94.3
1N HNO ₃ +0.2M ascorbic acid	0.545	35.3
3N HCl+0.2M ascorbic acid	15.71	94.0
1M H ₂ C ₂ O ₄ +0.2M ascorbic acid	23.32	95.9
1M H ₂ SO ₄ +0.2M ascorbic acid	31.37	96.9

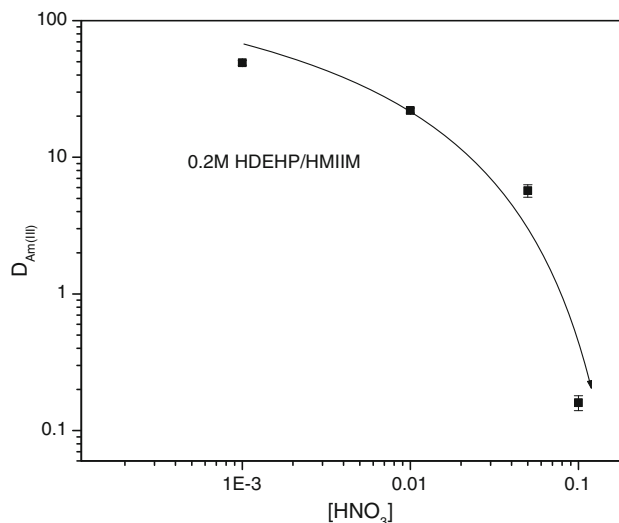
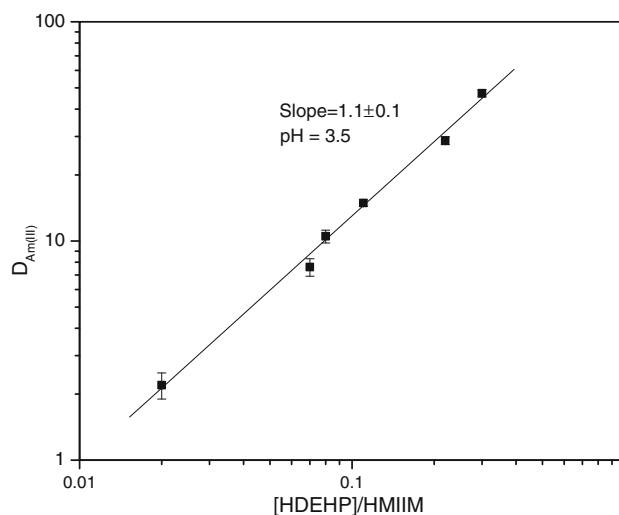
The change in entropy (ΔS) was found out by the equation $\Delta G = \Delta H - T\Delta S$.

The thermodynamic values ΔG , ΔH and ΔS are given in Table 2. These constants computed using concentrations rather than activities of the various species involved in the extraction equilibria are not true thermodynamic quantities. Under conditions of constant concentration of acid and the extractants, the contributions of activity coefficients to the thermodynamic values should be fairly constant, rendering the values (Table 2), reliable for relative, if not absolute comparisons. It was observed that the extraction reaction is favored by negative ΔH and counteracted by negative ΔS . The entropy gain during the removal of water molecule is not fully compensated by the entropy loss on complex formation with HDEHP and therefore a small negative ΔS . Even though the extraction is counteracted by negative ΔS value the overall reaction is favored by negative free energy change (ΔG). It is known that thermodynamic values derived from small range of temperatures are more precise and therefore small differences of temperatures were considered for *D* measurements.

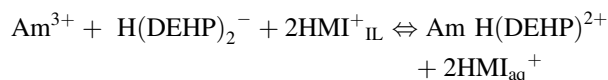
Back extraction studies of Pu(IV) loaded with HDEHP in RTIL were carried out by employing different reagents. From the results given in Table 3 it can be seen that strippants like 1M oxalic acid, 3N HCl+0.2 M ascorbic acid, 1M oxalic acid+0.2M ascorbic acid, 1M H₂SO₄+0.2M ascorbic acid gave nearly quantitative back extraction.

Extraction of Am(III)

Extraction studies of Am(III) were carried out by employing one of the above mentioned RTIL viz. HMIIM and HDEHP as the extractant. From the initial studies, it was observed that the extraction of Am(III) was poor in acidic range (1M and above) and the distribution ratio (*D*) was found to be negligible. Therefore the extraction was carried out from aqueous phase below 0.1M nitric

**Fig. 4** Effect of [HNO₃] on *D*_{Am(III)}**Fig. 5** Log–log plot of *D*_{Am(III)} versus [HDEHP]/HMIIM

acid. It was seen that the *D* ratio increases with decrease in nitric acid molarity (Fig. 4). The effect of [HDEHP] on the extraction of Am(III) from pH 3 was studied and *D* values were plotted against [HDEHP] (Fig. 5). From the slope of the graph it was inferred that 1 molecules of HDEHP takes part in the extraction reaction. The extraction reaction can be written as



Extraction reaction is assumed to be through cation exchange process similar to the extraction of Pu(IV) by HDEHP in RTIL. From our studies, it was observed that by using 1–2M HNO₃ quantitative extraction of Pu(IV) could

be possible by employing HDEHP as extractant. But on the other hand, the extraction of Am(III) was found to be very poor under the same conditions. This is useful in separating Pu(IV) from Am(III). The back extraction of Am(III) from RTIL phase in the present case can be done by using 1–2M nitric acid as strippant.

Conclusions

From the distribution ratio (D), it was seen that all the three RTILs used were good for the extraction of Pu(IV). From the slope analysis, it was inferred that the extraction was through cation exchange mechanism. Under the acidic conditions, the extraction of Am(III) was found to be poor, but it could be increased by carrying out the extraction at 2–3 pH conditions. This is useful in separating Pu(IV) from Americium(III). The stoichiometry of the extracted complexes of Pu(IV), Am(III) were inferred as $[\text{PuH}(\text{DEHP})_2]^{3+}$, $\text{AmH}(\text{DEHP})^{2+}$ respectively. It also indicated the role of RTIL anions for charge neutralization in both cases. The effect of temperature on the extraction reaction indicated that the extraction reaction was favored by negative enthalpy change and counteracted by negative entropy change. But the extraction reaction was favored by over all negative free energy change. It was also observed that stripping of Pu, Am from RTIL phase could be accomplished by employing proper reagents.

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