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Extractive complexation of lanthanides and Am(III) by 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone in ionic liquid: Solvent extraction and spectroscopic studies

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ABSTRACT

Extraction behaviour of trivalent actinides and lanthanides was studied using solutions of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP), a beta-diketone, in a room temperature ionic liquid, 1-methyl-3-octylimidazolium bis(trifluoromethylsulphonyl) imide ($C_8mim \cdot Tf_2N$). The complex extracted into $C_8mim \cdot Tf_2N$ differs in its composition than those observed in molecular diluents such as benzene. Whereas, neutral ML_3 complex is predominant in molecular diluents, a positively charged complex, $[ML_2 \cdot HL]^+$ (where M = La^{3+}, Eu^{3+}, Lu^{3+} and Am^{3+}; L = $PMBP^-$; HL = HPMBP), was identified to be extracted into the ionic liquid medium. Luminescence spectroscopic studies suggested presence of four inner-sphere water molecules in the extracted species. This paper reports for the first time the stability constant of a lanthanide (Nd^{3+}) complex with HPMBP in $C_8mim \cdot Tf_2N$ which are significantly larger than those reported in molecular diluents. Thermodynamic parameters were also determined to throw light on the nature of complexation.

1. Introduction

Rare earth elements (REE) are moderately abundant in the earth's crust, some even more abundant than copper, lead, gold, and platinum [1]. While more abundant than many other minerals, REE elements are not concentrated enough to make them easily exploitable economically. Global demand for REE is expected to be around 30,000 tons annually and meeting this target will be a difficult task, given the economic implications on their production from minerals and ores [1]. Some of the major end users of REE include automotive catalytic converters, fluid cracking catalysts in petroleum refining, phosphors in screen displays, molecular magnets, rechargeable batteries for hybrid electric vehicles, and numerous medical applications such as contrast enhancing agents in NMR imaging and luminescent probes [2]. Due to similarities in their chemical properties with those of trivalent actinides, separation of lanthanides, either mutually or as a group from actinides, is one of the most challenging tasks for the researchers working in this fascinating area. Separation of lanthanide elements from minor actinides has relevance in studies related to transmutation of long-lived toxic radio-isotopes (into shorter lived) present in nuclear wastes from the P & T (Partitioning and Transmutation) strategic viewpoint [3].

Several classes of reagents such as beta diketones, diglycolamides and soft ligands with *N* and *S* donor groups in molecular diluents have been used for the separation of lanthanides from various aqueous streams [4]. The work on relatively new diluents, room temperature ionic liquids (RTILs) with these reagents is rather sparse, and such studies only report the extraction data without explaining insight into the complexation. RTILs are known to have certain advantages such as negligible vapor pressures, long liquidus range, solubilizing ability to many organic/inorganic compounds and availability in numerous combinations with varying physicochemical properties [5]. Their potential ability to replace the toxic volatile organic compounds and unusually high extraction efficiencies with a variety of mechanisms renders them attractive from both basic as well as application point of view. The extraction mechanisms in RTILs vary depending on several factors and are fascinating to study [6]. For example, in $C_{10}mimNTf_2$ (1-methyl-3-decylimidazolium derivative), the mechanism was shown to be of solvation type which involved the extraction of a neutral species similar to those reported in non-polar molecular diluents such as *n*-dodecane [7]. On the other hand, in $C_8mimNTf_2$ (1-methyl-3-octylimidazolium derivative), both solvation and cation-exchange mechanisms have been reported and in analogous ionic liquids with lower alkyl chain lengths, the mechanism was reported to be predominantly cation-exchange [8]. When solutions of HTTA (2-thenoyltrifluoroacetone) in $C_4mimNTf_2$ (1-methyl-3-butylimidazolium derivative) were used for the extraction of lanthanide ions, the extraction mechanism conformed to an anion-exchange mechanism [9].

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Among the various ligands used for extracting the trivalent *f*-elements (lanthanides and actinides), beta-diketones, particularly those consisting of the acyl pyrazolone moieties with different substituents and pKa values in the range of 2.5–4 are quite interesting [4a]. Among these, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP), a monobasic chelating ligand, which displays keto-enol tautomerism (Fig. S1, Supporting Information), has been well studied for lanthanide and actinide ion extraction in molecular diluents [10]. There are few reports on the extraction of lanthanides by HPMBP alone or in combination with neutral donor ligands in RTILs [11]. However, these reports are not extensive and do not contain fundamental thermodynamics data on understanding the complexation in RTILs. In view of different possible extractive complexation mechanism with HPMBP in RTIL, it was of interest to carry out studies on the extractive complexation of three extreme lanthanide ions, viz. light, middle and heavy (La^{3+}, Eu^{3+} and Lu^{3+}) and a representative trivalent actinide ion (such as Am^{3+}) with this ligand in RTIL. The focus of this work was to understand the mechanistic aspects of the extraction/complexation of the HPMBP/$C_8mim \cdot Tf_2N$ system vis-à-vis the molecular diluents. Detailed experimental procedures are given in the supporting information.

1.1. Liquid–liquid extraction studies

It was often found that RTILs, especially those containing imidazolium cations and common anions (PF_6^-, $N(SO_2CF_3)_2^-$ etc.) have relatively higher viscosity as compared to molecular diluents [6a]. Since, the mass transfer in liquid-liquid extractions were usually influenced by viscous liquids, thus, the rates of extraction are expected to be relatively slower in RTILs as compared to molecular solvents [12]. In view of this, the kinetics for the extraction was obtained in the present study by measuring the *D* values of metal ions as a function of time of equilibration. It was noted that approximately 30 minutes were required to reach the equilibrium D_M (distribution ratio of the metal ion M^{3+}) value for all the metal ions studied, viz. La^{3+}, Eu^{3+}, Lu^{3+} and Am^{3+} (Fig. S2, Supporting Information). As expected, the extraction kinetics was significantly slower in $C_8mim \cdot Tf_2N$ than with extractants in molecular diluents such as *n*-dodecane where extraction kinetics was faster (<5 min) [11b]. A detailed study pertaining to the slow extraction kinetics in RTILs has been studied previously using diglycolamide based extractants [12]. The extraction kinetics of a metal ion from the aqueous phase to the organic phase can broadly be divided into two stages, (i) complex formation at the RTIL/aqueous interface, and (ii) the subsequent diffusion of the complex into the bulk of the RTIL phase. The diffusion step in RTILs is relatively slow due to the high viscosity of the medium which is reflected in the overall slow extraction kinetics. However, it is important to mention that the anomalous faster extraction kinetics has also been reported in RTILs, which was ascribed to a few other factors overriding the viscosity effect [12].

Table 1
Results of slope analysis in the solvent extraction studies for the determination of the number of ligand molecules (x) present in the M^{3+}/HPMBP complex and the number of protons (y) c process.

Metal ions	Value of ‘x’	Value of ‘y’	Probable species
La^{3+}	3.2	2.0	$[La(HPMBP)(PMBP)_2(H_2O)_x]^+$
Eu^{3+}	3.3	2.1	$[Eu(HPMBP)(PMBP)_2(H_2O)_x]^+$
Lu^{3+}	3.2	2.0	$[Lu(HPMBP)(PMBP)_2(H_2O)_x]^+$
Am^{3+}	3.4	2.1	$[Am(HPMBP)(PMBP)_2(H_2O)_x]^+$

The extraction behaviour of metal ions with HPMBP can be best predicted utilizing the Eq. (1) (for details of derivation, see Supporting Information).

$$\log D_M = \log K_{ex} + x \log[HL]_{(IL)} + y\ pH \qquad (1)$$

where Kex is the two phase extraction constant and the subscript '(IL)' indicates species in the ionic phase A plot of log D_M vs. ligand concentration in $C_8mim \cdot Tf_2N$ phase at constant aqueous pH would give an idea about the number of ligands associated in the complex. Similarly, a plot of log D_M vs. pH of the aqueous phase at fixed HPMBP concentration will give information on the number of protons released in the complexation process. Fig. 1 shows the log D_M vs. pH plots for all the metal ions studied. At any pH below 2.5, the order of extraction was $Lu^{3+} > Eu^{3+} > Am^{3+} > La^{3+}$. This order for lanthanides was expected following the ionic potential of these metal ions. At higher pH, the D_M values merged together for all except La^{3+} which displayed a clear and distinct curve from other metal ions. The overall curve in the figure could be explained following a pH dependent dissociation of HPMBP. It should be mentioned here that the pK_a of HPMBP in ionic liquid media was unavailable till recently. Atanassova, et al. [13] recently conceptualized and determined pK_a of beta diketones in a few RTIL. If the value is taken as ~2.5 in $C_8mimNTf_2$, it can be seen that at lower pH (<2.5), the dissociation of HPMBP was insignificant, resulting in lower concentration of the dissociated form of the HPMBP, and consequently, the D_M

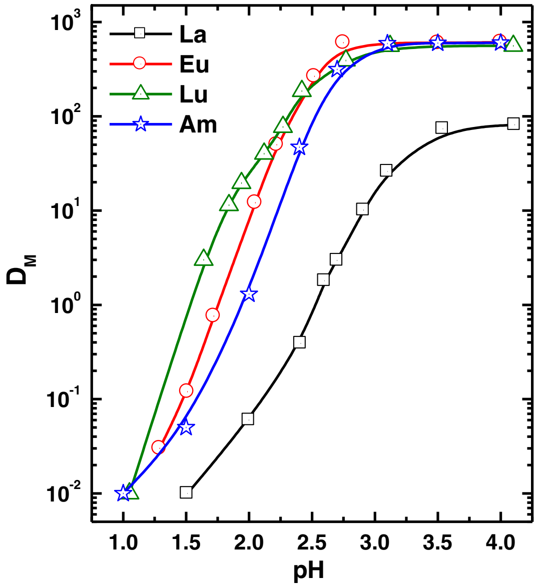

Fig. 1. Extraction profiles of metal ions as a function of aqueous phase pH. Organic phase: 10 mmol/L HPMBP in $C_8mim \cdot Tf_2N$.

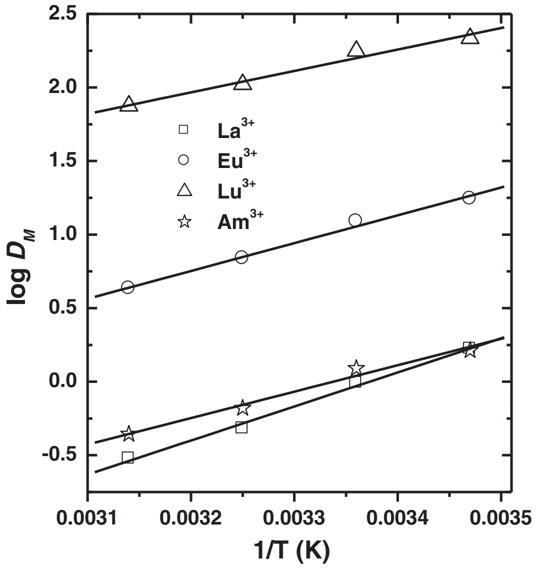

Fig. 2. van't Hoff plot for determination of enthalpy of extraction of lanthanides from by HPMBP. Organic phase: 10 mmol/L HPMBP in $C_8mim \cdot Tf_2N$; aqueous phase: pH 2 (HNO_3).