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Superbase-derived protic ionic liquids with chelating fluorinated anions

Jason R. Bell[a], Huimin Luo[a,*], Sheng Dai[b]

[a] Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6181, United States
[b] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6201, United States

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ABSTRACT

Eighteen new protic ionic liquids were synthesized in one step from five organic superbases and five commercially available fluorinated β-diketones. Physical properties of the ionic liquids, including thermal decomposition temperature were determined. Nine of the ionic liquids were examined as extraction media for La^{3+}, with some very large distribution coefficients obtained.

Interest in ionic liquids for separation processes has grown rapidly in the last two decades. Ionic liquids possess properties that make them excellent candidates for separations, including tunable polarity, hydrophobicity or hydrophilicity, low vapor pressure, and high thermal stability.[1] Specifically, the use of ionic liquids for the extraction of metal ions from aqueous solutions has been of significant interest.[2] Hydrophobic ionic liquids with dissolved neutral ligands such as crown ethers,[3] diamides,[4] alkylphosphates and phosphine oxides,[5] and β-diketones[6] have been studied, and it has been shown that ionic liquids can improve metal ion separations by several orders of magnitude over conventional solvents.[3a,7] Due to the ease of functionalizing the imidazolium cation, task-specific ionic liquids with diverse and complex chelating functionality have been synthesized.[8] Examples of the functional groups incorporated include urea,[9] acetylamine,[10] phosphoryl,[11] polyethers,[12] crown ether,[13] hydroxybenzylamine.[14] Though a wide array of ILs with functionalized cations has been synthesized, none have proven to be exceptionally better than the conventional ILs with dissolved neutral extractants. Task-specific ionic liquids with functional anions are quite less common, with salicylate-type anions,[15] and fluorinated β-diketones[16] being the most common for extraction applications.

β-Diketones have been utilized extensively as ligands for the extraction of metal cations, including lanthanides and actinides, into conventional organic solvents. Batzar found that the extraction efficiency of these ligands was inversely related to the pK_a of the β-diketone.[17] This is due to the more acidic diketone exhibiting a higher degree of enolate character, which is the necessary structure for ligating the metal cation. Therefore, the most efficient β-diketones for extraction are also the best candidates for a protic ionic liquid system,[18,19] in which the β-diketone conjugate base would perform as the functional IL anion. An aprotic IL containing the hexafluoroacetylacetonate anion (hfac) was reported to be immiscible with water, and a qualitative test showed the IL to be highly efficient at extracting Nd^{3+}, Cu^{2+}, and Co^{2+}.[16] The IL was, however, synthesized by a multistep process involving anion metathesis of an IL halide salt and ammonium hexafluoroacetylacetonate. Protic ILs utilizing fluorinated β-diketones and tertiary amines have also been reported,[20] synthesized through a simple one pot neutralization reaction, though none were examined for extraction capabilities.

Protic ionic liquids utilizing strong bases (i.e., organic ‘superbases’[21]) have been shown to have lower vapor pressures and superior thermal stabilities compared to typical protic ionic liquids using amine bases.[18] This is in accord with Angell and co-workers who found the vapor pressure of a protic IL varies inversely with the pK_a difference of the acid/base components.[22] Therefore we sought to investigate task-specific protic ionic liquids, utilizing organic superbases and fluorinated β-diketones as the cationic and anionic components, respectively. This would allow for a facile synthesis of a functionalized IL with high thermal stability.[18] Three commercially available superbases were used, two phosphazene bases: *tert*-butylimino-tri(pyrrolidino)phosphorane (P_1-*t*-Bu) and tetramethyl(tris(dimethylamino)phosphoranylidene)phosphorictriamid-ethyl-imin (P_2-Et), and the bicyclic guanidine base 7-methyl-1,5,7-triazabicyclo[4,4,0]dec-5-ene (MTBD). Two other organic superbases, 7-butyl-1,5,7-triazabicyclo[4,4,0]dec-5-ene (BTBD)[23] and 1,3-dimethyl-2-(1-butylimino)imidazolidine (BuG5)[24] were synthesized and used. The fluorinated β-diketones

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[*] Corresponding author.
E-mail address: luoh@ornl.gov (H. Luo).

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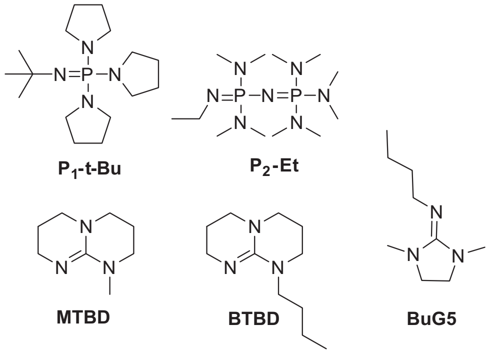

Figure 1. Superbases used in synthesis of ILs.

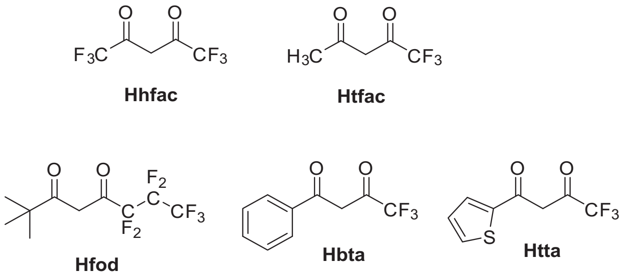

Figure 2. Fluorinated diketones used for synthesis of ILs.

were all commercially available and include 1,1,1,5,5,5-hexafluoroacetylacetone (Hhfac), 1,1,1-trifluoroacetylacetone (Htfac), 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octadione (Hfod), benzoyl-1,1,1-trifluoroacetone (Hbta), and 2-thenoyltrifluoroacetone (Htta). Their molecular structures are shown in Figures 1 and 2, respectively. Though 25 acid/base combinations were possible, only 18 ILs were synthesized. Further work with P$_1$-*t*-Bu was avoided due to the high melting points of initial ILs made with that base. MTBD and Htfac were avoided due to the water miscibility of their ILs.

The new task-specific protic ionic liquids were synthesized in high yield in a one step neutralization process. The superbase was cooled in an ice bath, and exactly one equivalent of fluorinated β-diketone was added dropwise with stirring. In the case of solid β-diketones, Hbta and Htta, the addition was reversed. The liquid base was added slowly to the solid β-diketone in the reaction vial. No purification was necessary for the neat ILs. For example, to a 5 mL conical vial under argon atmosphere, P$_2$-Et (1.0326 g, 3.042 mmol) was added, Hfod (708 μL, 3.042 mmol) was then added slowly via syringe while stirring.

NMR spectra of the ILs show an essentially independent behavior of the cation and anion. For each β-diketonate anion, a single proton resonance exists, independent of the cation. For example, the [hfac] anion resonance occurs as a singlet at approximately 5.66 ppm for all ILs. The transferred H$^+$ was observable in the region between 8 and 10 ppm for all ILs except those utilizing phosphazene bases, for which the transferred protons were not observed.

The physical properties of the ILs studied are compiled in Table 1. The thermal properties of ILs were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal decomposition temperatures range from 145 °C to 307 °C. This was typically greater than other PILs based on fluorinated β-diketones and tertiary amines.[20b] The [hfac] anion exhibited a distinctly higher thermal stability than [fod], a trend which was observed in the earlier work.[20b] The bicyclic guanidine cations, [MTBDH] and [BTBDH], showed better stability than all other cations, except for [P$_2$-EtH] which was significantly higher. The melting points of the ILs were strongly correlated to the anion. The [hfac] anion gave crystalline products with three of the five cations, whereas the [fod] anion gave only one. Both of the solid β-diketones, Hbta and Htta, gave solid salts with BuG5. [BuG5H][fod] was a liquid at all times during this study, even after refrigerated storage, however DSC shows a cold crystallization temperature at 26 °C, with a concomitant melting at 34.5 °C.

The viscosities of these ILs, as expected, decreased drastically with increasing temperature. ILs containing the bicyclic guanidinium cations [BTBDH] and [MTBDH] were very viscous. The [BuG5H] and [P$_2$-EtH] cations gave moderate values for viscosity, however one example, [BuG5H][hfac] gave a low viscosity, similar to many aprotic ILs, of 66.1 cP.

All ILs in this study were immiscible with water, except for [MTBDH] and [tfac] containing ILs. In order to study the extraction efficiency of the ILs, a 100 μL sample of each of the liquid ILs was vortexed for 60 min with 1.00 mL of 500 ppm La(NO$_3$)$_3$ solution. After the layers were separated by centrifugation for 5 min, the metal concentration in the aqueous phase was measured by ion chromatography (IC). Distribution coefficients can be calculated from La^{3+} concentrations in the aqueous phase before and after contacting with ILs and are listed in Table 2. For three of the nine

Table 1
Physical properties of ILs

IL	T_m (°C)	T_g (°C)	T_{dec} (°C)	Density (g/mL)	Viscosity 23 °C, cP	Viscosity 40 °C, cP
[MTBDH][hfac]	55	–	289	–	–	–
[MTBDH][fod]	–	−44	179	1.46	935	199
[BTBDH][hfac]	–	−46	261	1.43	538	136
[BTBDH][fod]	–	−41	198	1.32	>1500	369
[BTBDH][tfac]	–	−47	186	1.30	>1500	425
[BTBDH][bta]	–	−40	194	1.38	>1500	331
[BTBDH][tta]	–	−43	195	1.36	>1500	255
[BuG5H][hfac]	–	−68	250	1.42	66.1	27.9
[BuG5H][fod]	34.5	−51	145	1.38	446	122
[BuG5H][tfac]	–	−66	169	1.28	190	68.4
[BuG5H][bta]	48	–	180	–	–	–
[BuG5H][tta]	86	–	199	–	–	–
[P$_2$-EtH][hfac]	70	–	307	–	–	–
[P$_2$-EtH][fod]	–	−68	274	1.33	323	122
[P$_2$-EtH][bta]	–	−57	268	1.28	509	177
[P$_2$-EtH][tta]	–	−68	184	1.32	211	84.8
[P$_1$-*t*-BuH][hfac]	52	–	193	–	–	–
[P$_1$-*t*-BuH][fod]	69	–	191	–	–	–

Table 2
Distribution coefficients of La^{3+} using ILs for biphasic extraction

IL	D_{La}
[BTBDH][hfac]	130
[BuG5H][hfac]	48
[BTBDH][fod]	3900
[BuG5H][fod]	2200
[P_2-EtH][fod]	$>10^4$
[BTBDH][bta]	4000
[P_2-EtH][bta]	7700
[BTBDH][tta]	$>10^4$
[P_2-EtH][tta]	$>10^4$

ILs, the residual aqueous lanthanide concentration was below the limits of detection of the instrument, which yields a distribution coefficient (D_M) of $>10^4$. Extraction efficiency was seen to increase for larger and more hydrophobic anions, such as [fod] and [tta], which is consistent with our previous research on anion effects.[3b] Large hydrophobic cations, such as [P_2-EtH] and [BTBDH] also gave better extraction efficiencies. Note that this is in contrast to the cation exchange mechanism reported by Dietz,[3c] in which a conventional IL with a neutral extractant was used, and it was observed that distribution coefficients decreased with increased cation hydrophobicity. The extraction mechanism for this system has yet to be determined, and is the subject of current studies.

In conclusion, we have shown that task-specific protic ionic liquids can be easily synthesized in one step from commercially available organic superbases and fluorinated β-diketones. These ionic liquids are hydrophobic, have a wide liquid temperature range, have a thermal stability comparable to aprotic ionic liquids, and are able to extract lanthanide cations from aqueous solutions with high efficiency.

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Supplementary data

Supplementary data (experimental procedures for the synthesis of BTBD, BuG5, ILs, as well as ^1H NMR data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.05.037.

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