Room-temperature ionic liquids based on quaternary ammonium and their use for solvent extractions

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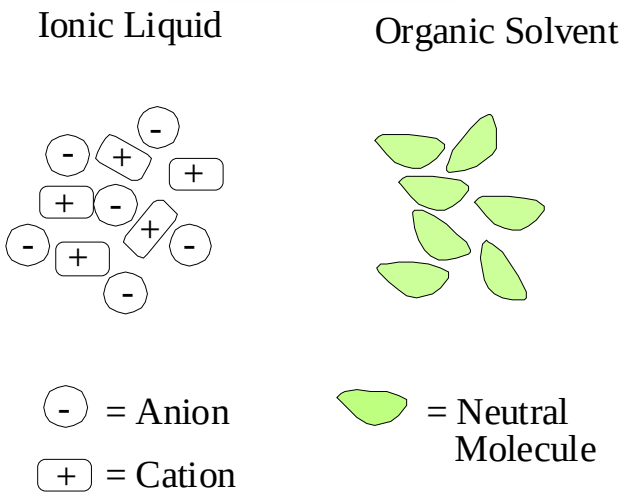
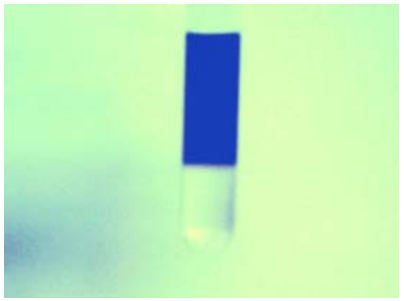
Why Ionic Liquids?

Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.

- ***Nonvolatility***
- ***Ionicity***
- ***Tunable Hydrophobicity***
- ***Tunable Lewis Acidity***
- ***Thermal Stability***
- ***Nonflammability***
- ***Wide Liquid-Phase Temperature.***
  (-100^{0}C to around 300^{0}C)

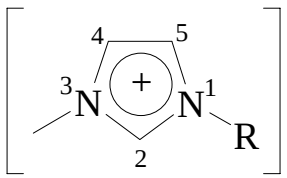




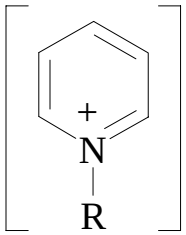
Photographic picture of the phase separation between an ionic liquid (molten salt) and an aqueous solution containing Cu(II) dye.

Range of organic cations and anions typically used to prepare room-temperature ionic liquids

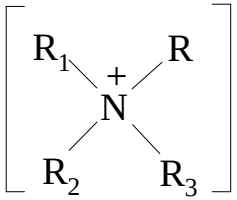
Most commonly used cations:



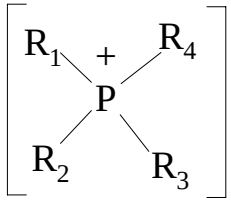
1-alkyl-3-methyl-imidazolium



N-alkyl-pyridinium



Tetraalkyl-ammonium



Tetraalkyl-phosphonium ($R_{1,2,3,4}$ = alkyl)

Some possible anions:

water-insoluble → water-soluble

$[PF_6]^-$
$[(CF_3SO_2)_2N]^-$
$[BR_1R_2R_3R_4]^-$

$[BF_4]^-$
$[CF_3SO_3]^-$

$[CH_3CO_2]^-$
$[CF_3CO_2]^-$, $[NO_3]^-$
Br^-, Cl^-, I^-
$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Most commonly used alkyl chains:

ethyl octyl
butyl decyl
hexyl

Comparison of Sr extaction results obtained using imidazolium-based ionic liquids and conventional Solvents

Ionic Liquid	D_{Sr}^{2+} With 0.15M crown ether
BuMeIm PF_6	2.4×10
$EtMe_2$ Im Tf_2N	4.5×10^3
EtMeIm Tf_2N	1.1×10^4
PrMeIm Tf_2N	5.4×10^3
Toluene	0.76
Chloroform	0.77

Extractant is >14000 times more effective in ionic liquid than in conventional solvent

Very high capture of cesium has been measured for imidazolium-based ionic liquids solvents

Cs Extraction Results* using BoBcalixC6 in Ionic Liquid Solvents

Concentration of BoBcalixC6 in $BuMeIm^+Tf_2N^-$	Initial aqueous phase composition	D_{K^+}	D_{Cs^+}	D_{Na^+} or $D_{Sr^{+2}}$	D_{Cs^+}/D_{K^+}
7.7×10^{-3} *M*	150 ppm K^+, Cs^+, and Na^+	3.7	162	0	44
7.7×10^{-3} *M*	150 ppm K^+ and Cs^+	2.8	118	-	43
7.7×10^{-3} *M*	150 ppm K^+, Cs^+, and Sr^{+2}	3.0	102	0	35

BoBcalixC6 Concentration	D_{Cs^+} *R* in $RMeIm^+Tf_2N^-$				chloroform
	Propyl	Butyl	Hexyl	Octyl	
1.3×10^{-2} *M*	140	130	57	18	0.034

*The distribution coefficient, D_M, is defined as $D_M = \frac{[Concentraton of\ M\ in carrier solution]}{[Concentraton of\ M\ in aqueous solution]}$.

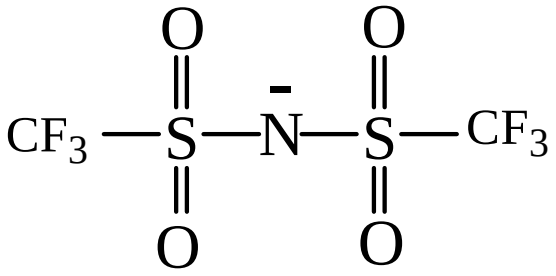
Extractant is >4000 times more effective in ionic liquid than in conventional solvent

Synthesis of quaternary ammonium-based ionic liquids

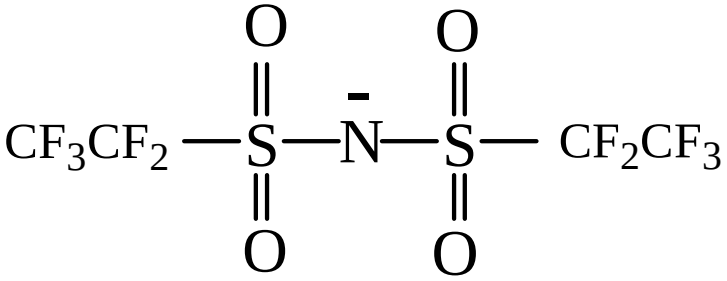
R= alkyl groups ranging from C_1 to C_{12}

A = NTf_2^- or $BETI^-$

NTf_2^-:



$BETI^-$:



These new ILs have similar physical properties as ILs with imidazolium as cations

ILs	Molecular Formula	Yield (%)	MP (°C)	T_{onset} (°C)	IL solubility in H_2O (mM)	Water content (ppm)	
						Dried	Wet[b]
1	$[(CH_3)_2(i\text{-}C_3H_7)NH][NTf_2]$	94	NA[c]	360	153	219	31900
2	$[(CH_3)_2(i\text{-}C_3H_7)NH][BETI]$	95	NA	340	31.2	193	24100
3	$[(CH_3)(C_2H_5)_2NH][NTf_2]$	93	NA	360	117	634	38400
4	$[(CH_3)(C_2H_5)_2NH][BETI]$	97	NA	340	25.1	448	19700
5	$[(CH_3)_2(n\text{-}C_4H_9)NH][NTf_2]$	97	NA	360	87.3	284	34600
6	$[(CH_3)_2(n\text{-}C_4H_9)NH][BETI]$	94	36	300	NA	NA	NA
7	$[(C_2H_5)_3NH][NTf_2]$	97	NA	360	95.7	453	27800
8	$[(C_2H_5)_3NH][BETI]$	97	NA	340	14.1	131	22700
	$[C_4mim][PF_6]$		NA	395	86.6	513	20700
	$[C_4mim][NTf_2]$		NA	420	19.0	240	13600
	$[C_4mim][BETI]$		NA	400	3.41	143	7070

Physical properties of ionic liquids(2)

ILs	Molecular Formula	Yield (%)	MP (°C)	T_{onset} [a] (°C)	IL solubility in H_2O (mM)	Water content (ppm)	
						Dried	Wet[b]
9	$[(CH_3)(n\text{-}C_3H_7)_2NH][NTf_2]$	96	NA	350	20.6	530	13600
10	$[(CH_3)(n\text{-}C_3H_7)_2NH][BETI]$	98	64	300	NA	NA	NA
11	$[(C_2H_5)_2(n\text{-}C_4H_9)NH][NTf_2]$	94	NA	335	35.4	299	35600
12	$[(C_2H_5)_2(n\text{-}C_4H_9)NH]$ [BETI]	96	NA	310	27.6	220	17100
13	$[(C_2H_5)(i\text{-}C_3H_7)NH][NTf_2]$	91	NA	350	52.9	220	21700
14	$[(C_2H_5)(i\text{-}C_3H_7)NH]$ [BETI]	96	36	330	NA	NA	NA
15	$[(n\text{-}C_3H_7)_3NH][NTf_2]$	93	49	350	NA	NA	NA
16	$[(n\text{-}C_4H_9)_3NH][NTf_2]$	93	37	335	NA	NA	NA
	$[C_6mim][PF_6]$		NA	365			
	$[C_6mim][NTf_2]$		NA	425			
	$[C_6mim]$[BETI]		NA	405			

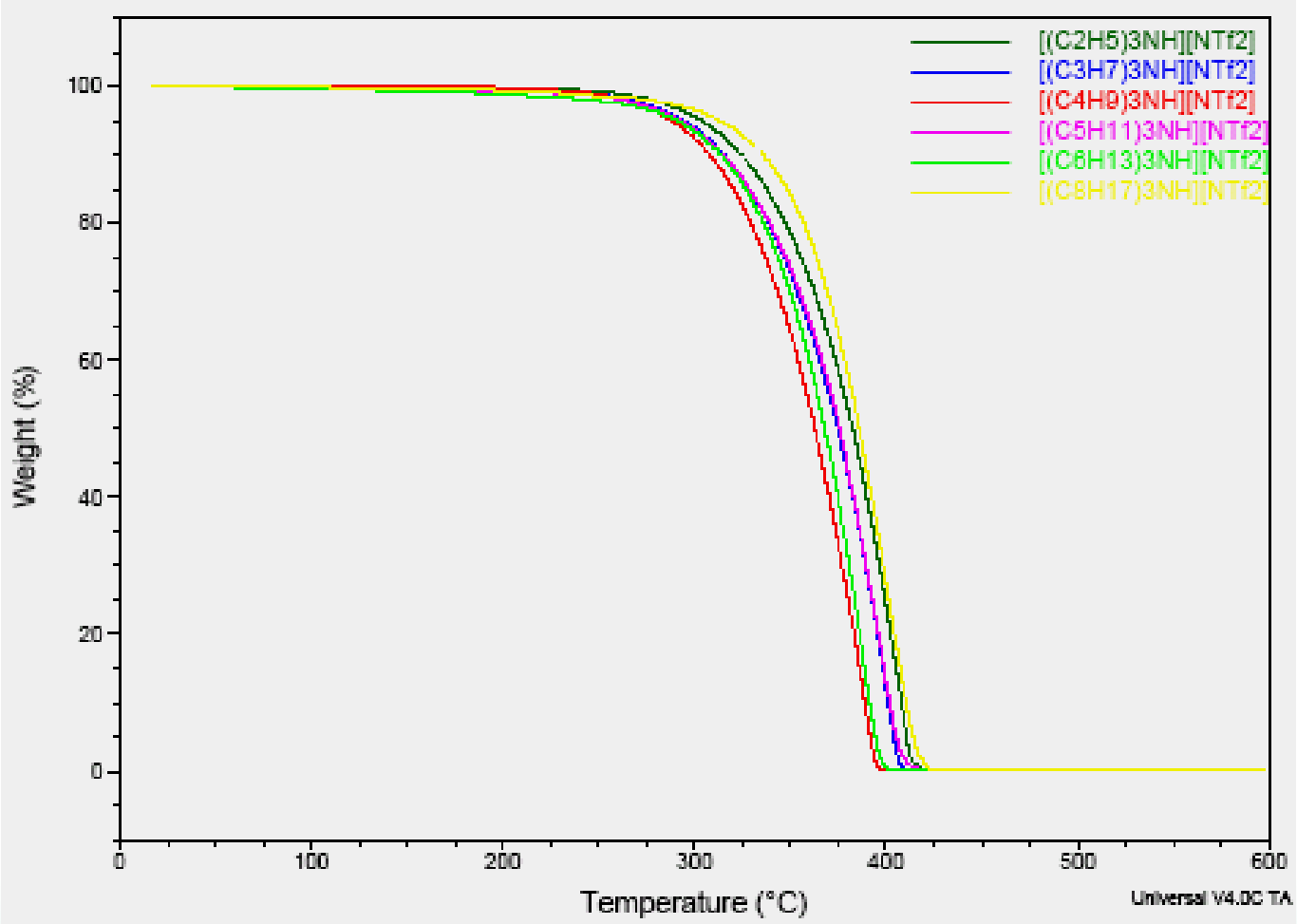
Physical properties of ionic liquids(3)

ILs	Molecular Formula	Synth. Yield (%)	MP (°C)	T_{onset} [a] (°C)	IL solubility in H_2O (mM)	Water content (ppm)	
						Dried	Wet[b]
17	$[(i\text{-}C_4H_9)_3NH][NTf_2]$	95	62	315	NA	NA	NA
18	$[(n\text{-}C_6H_{13})_3NH][NTf_2]$	93	NA	345	37.0	429	13000
19	$[(n\text{-}C_8H_{17})_3NH][NTf_2]$	99	NA	360	19.6	232	11600
20	$[(CH_3)_2(n\text{-}C_{12}H_{25})NH]$ [NTf2]	98	NA	378	6.55	1396	19100
21	$[(n\text{-}C_4H_9)NH_2][NTf_2]$	92	62	310	NA	NA	NA
22	$[(n\text{-}C_6H_{13})NH_2]$ $[NTf_2]$	92	87	320	NA	NA	NA
23	$[(n\text{-}C_8H_{17})NH_3][NTf_2]$	95	NA	350	96.0	2285	63100
24	$[(n\text{-}C_8H_{17})NH_3]$[BETI]	96	NA	325	17.9	608	17300

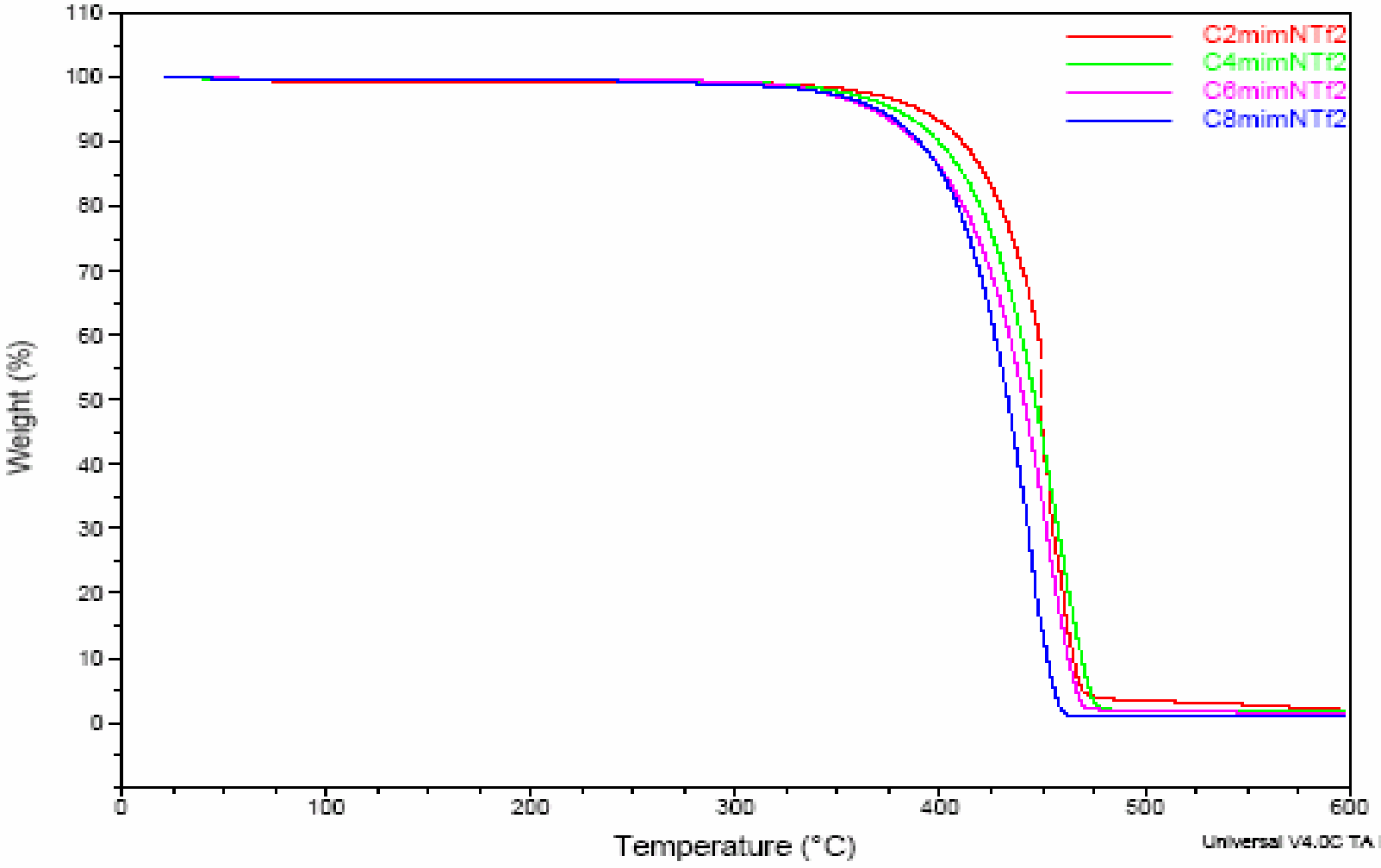
Thermal stabilities of these ILs seem to be independent of the carbon chain length of alkyl groups on ammonium cations

ILs	Physcical state at RT	MP(˚C)	T_{onset} (˚C)
$[(C_2H_5)_3NH][NTf_2]$	liquid	NA	355
$[(n\text{-}C_3H_5)_3NH][NTf_2]$	solid	49	335
$[(n\text{-}C_4H_9)_3NH][NTf_2]$	solid	37	335
$[(n\text{-}C_5H_{11})_3NH][NTf_2]$	solid	30	340
$[(n\text{-}C_6H_{13})_3NH][NTf_2]$	liquid	NA	340
$[(n\text{-}C_8H_{17})_3NH][NTf_2]$	liquid	NA	355

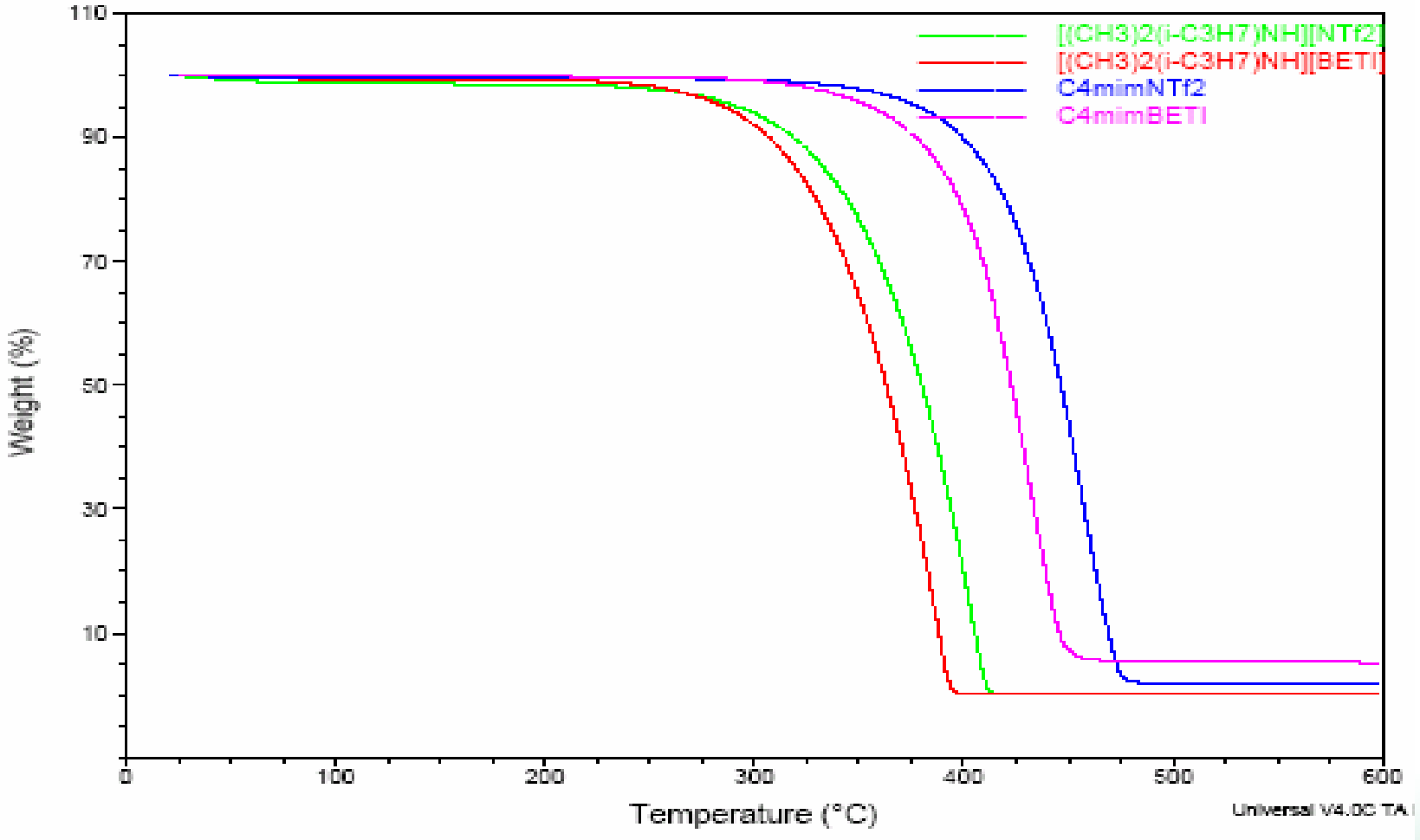
TGA plots of selected ammonium-based ILs



TGA plots of imidazolium based ILs



ILs with quaternary ammonium cation exhibit slightly lower thermal stabilities than imidazolium-based ILs



ILs with quaternary ammonium cations have similar viscosity as imidazolium-based ILs

ILs	Molecular Formula	Molecular Weight	Density (g/mL)	Viscosity (cP)		
				23°C	40°C	100°C
1	$[(CH_3)_2(i\text{-}C_3H_7)NH][NTf_2]$	368.3	1.42	67.72	29.93	6.194
2	$[(CH_3)_2(i\text{-}C_3H_7)NH][BETI]$	468.3	1.53	216.7	81.19	9.967
3	$[(CH_3)(C_2H_5)_2NH][NTf_2]$	368.3	1.43	46.42	23.31	5.328
4	$[(CH_3)(C_2H_5)_2NH][BETI]$	468.3	1.51	159.4	64.66	8.924
5	$[(CH_3)_2(n\text{-}C_4H_9)NH][NTf_2]$	382.3	1.39	55.69	25.97	5.246
7	$[(C_2H_5)_3NH][NTf_2]$	382.3	1.36	49.20	25.21	5.862
	$[C_4mim][NTf_2]$	419.38	1.42	50.72	25.30	5.849
	$[C_4mim]$ [BETI]	519.38	1.46	117.6	51.25	8.264
	$[C_6mim][NTf_2]$	446.35	1.33	68.98	34.42	6.818
	$[C_6mim]$ [BETI]	546.35	1.46	141.5	60.08	8.775

Density and viscosity of ionic liquids(2)

ILs	Molecular Formula	Molecular Weight	Density (g/mL)	Viscosity (cP)		
				23°C	40°C	100°C
8	$[(C_2H_5)_3NH][BETI]$	482.3	1.48	163.4	67.09	9.281
9	$[(CH_3)(n\text{-}C_3H_7)_2NH][NTf_2]$	396.3	1.34	61.40	27.95	5.434
11	$[(C_2H_5)_2(n\text{-}C_4H_9)NH][NTf_2]$	410.3	1.33	67.12	31.34	6.090
12	$[(C_2H_5)_2(n\text{-}C_4H_9)NH][BETI]$	510.3	1.42	158.4	64.28	8.773
13	$[(i\text{-}C_3H_7)_2(C_2H_5)NH][NTf_2]$	410.3	1.32	191.7	77.82	10.88
18	$[(n\text{-}C_6H_{13})_3NH][NTf_2]$	550.6	1.12	170.4	71.60	9.690
19	$[(n\text{-}C_8H_{17})_3NH][NTf_2]$	634.7	1.06	219.3	89.43	11.74
20	$[(CH_3)_2(n\text{-}C_{12}H_{25})NH][NTf_2]$	494.5	1.17	158.6	63.87	8.767
23	$[(n\text{-}C_8H_{17})NH_3][NTf_2]$	410.3	1.32	331.4	125.0	14.20
24	$[(n\text{-}C_8H_{17})NH_3][BETI]$	510.3	1.38	763.2	265.4	26.77

Summary for synthesis of quarternary ammonium-based Ionic Liquids

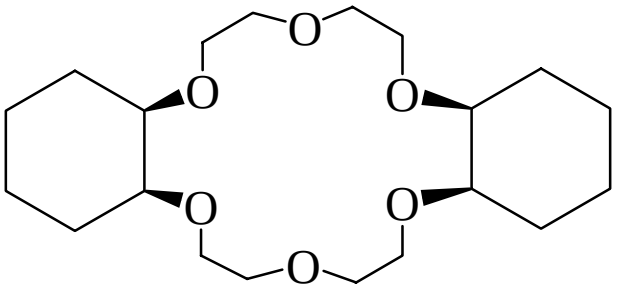
- Twenty four ILs based on quarternary ammonium cations have been synthesized.
- Sixteen of them are liquid at room temperature and the melting points of other eight ILs are all below 100˚C.
- Compared with imidazolium-based ILs, these ILs have:
    1. Higher solubility in water.
    2. Similar viscosity.
    3. Slightly lower thermal stability.

Extraction experiments

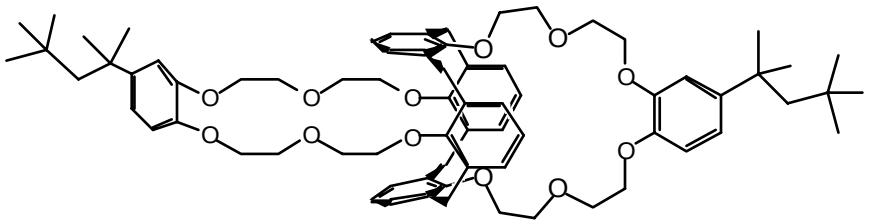
The extraction experiments were performed by contacting 1 mL of ionic liquids containing crown ether with 10 mL of CsCl or $SrCl_2$ (1.5×10^{-3} M) for about 1 hour in a vibrating mixer and. After centrifugation, the upper aqueous phase was separated, and the concentration of Cs^+ or Sr^{2+} was determined by ion chromatography.

$$D_M = \left\{ \frac{\left(C_i - C_f\right)}{\left(C_f\right)} \right\} \times \frac{\{Volume\ of\ \ aqueous\ solution\}}{\{Volume\ of\ \ IL\}} \qquad (1)$$

Structures of two extractants used in solvent extraction experiments



Dicyclohexane-18-crown-6



Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
"BoBCalixC6"

pH Affects on Cs extraction by BOBCalixC6 or DCH18C6 in these new ILs

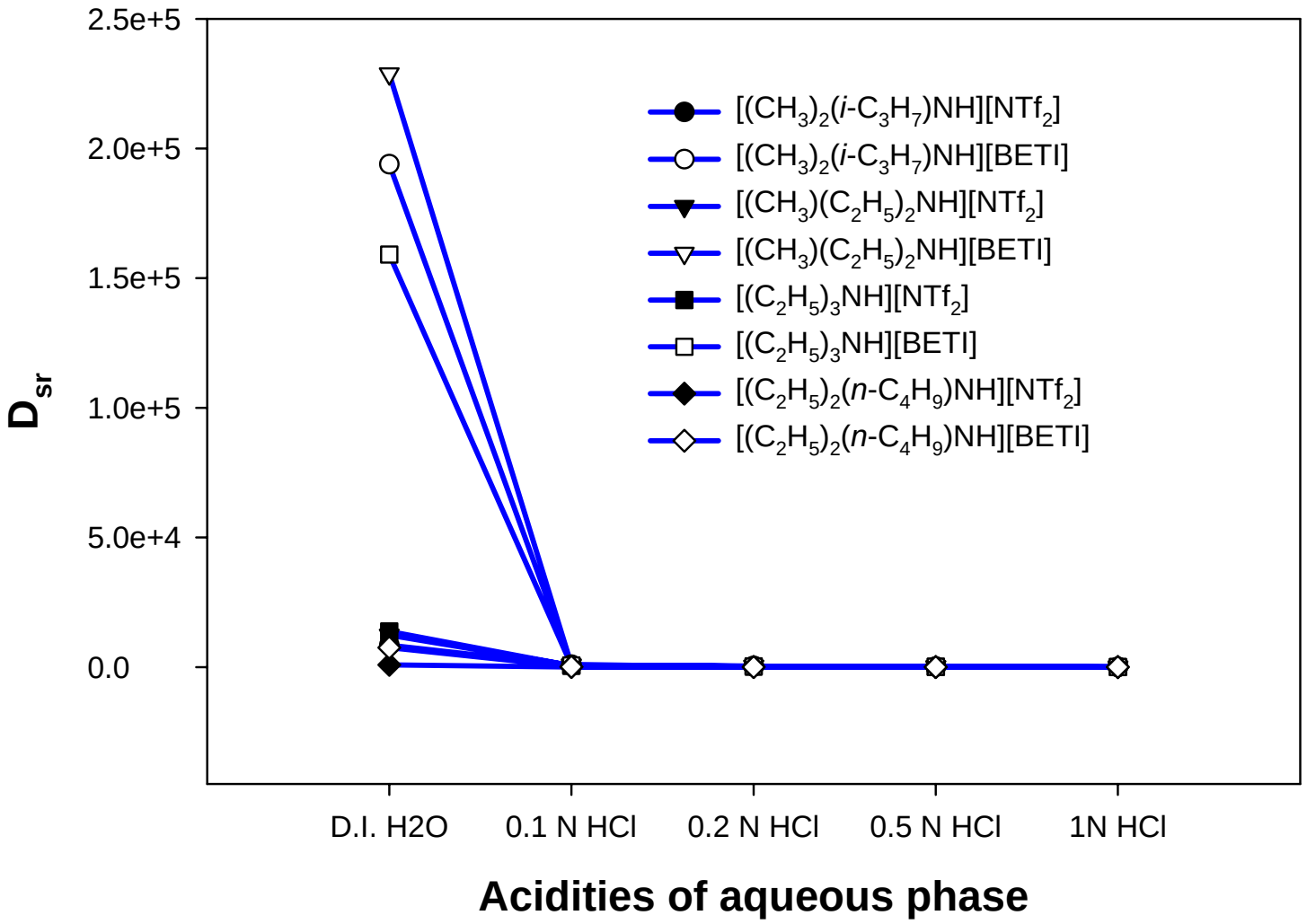
ILs	Molecular Formula	D_{Cs} at different pH conditions			
		7.6mMBOBCalixC6 1.5mM CsCl		100mM DCH18C6 1.5 mM CsCl	
		D.I. H_2O	0.1 N HCl	D.I.H_2O	0.1 N HCl
1	[(CH3)2(*i*-C3H7)NH][NTf2]	NA[a]	NA	154	13.8
2	[(CH3)2(*i*-C3H7)NH][BETI]	NA	NA	2610	18.8
3	[(CH3)(C2H5)2NH][NTf2]	NA	NA	709	18.2
4	[(CH3)(C2H5)2NH][BETI]	NA	NA	1330	23.4
18	[(*n*-C6H13)3NH][NTf2]	13.9	17.9	1.49	2.65
19	[(*n*-C8H17)3NH][NTf2]	9.78	22.9	0.62	3.13
20	[(CH3)2(*n*-C12H25)NH][NTf2]	10.3	14.9	1.37	2.90
	[C4mim][NTf2]	13.8		380	
	[C6mim][NTf2]	11.5		66.0	

[a] Limited Solubilities of BOBCalixC6.

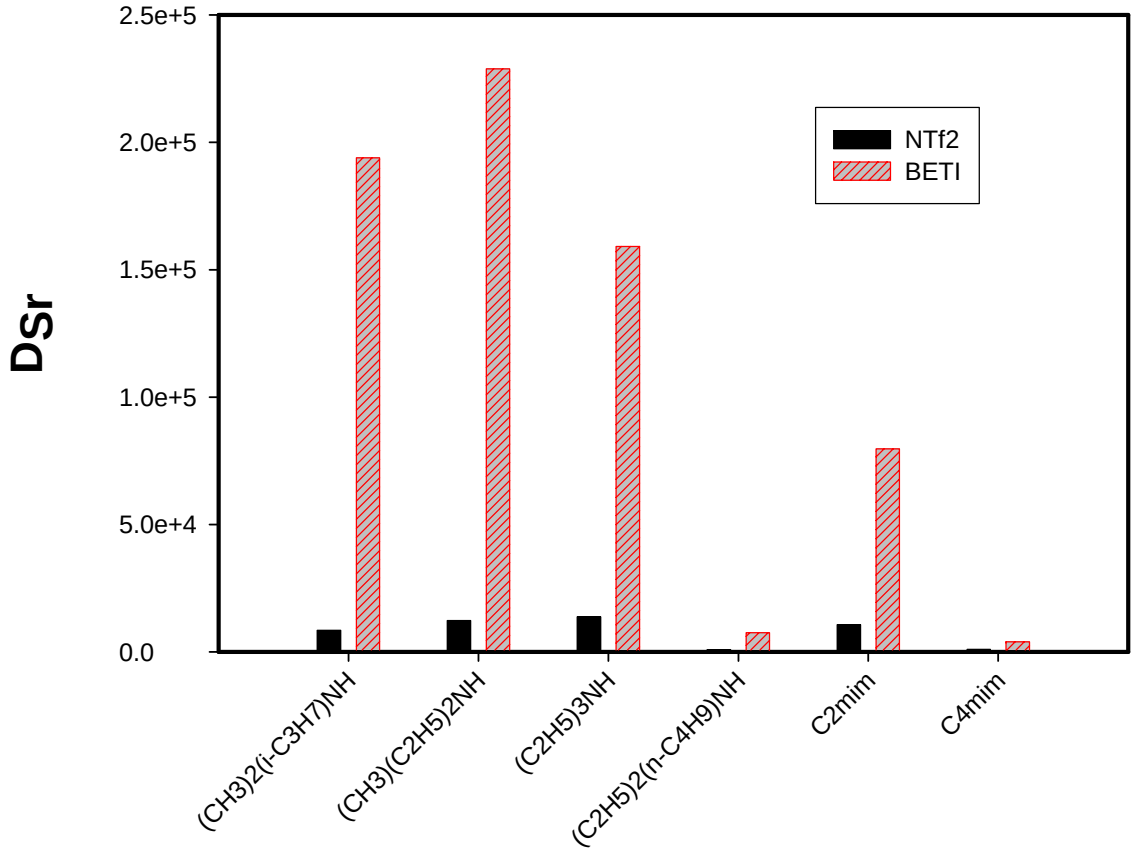
Effects of pH on D_{Sr} of ionic liquids containing 100 mM DCH18C6

ILs	Molecular Formula	D_{Sr} at different pH conditions				
		1.5 mM $SrCl_2$				
		D.I. H_2O	0.1 N HCl	0.2 N HCl	0.5 N HCl	1.0 N HCl
3	$[(CH_3)(C_2H_5)_2NH][NTf_2]$	12300	655	287	107	54.6
4	$[(CH_3)(C_2H_5)_2NH][BETI]$	229000	904	363	126	64.5
11	$[(C_2H_5)_2(n\text{-}C_4H_9)NH][NTf_2]$	870	82.3	34.4	17.6	10.6
12	$[(C_2H_5)_2(n\text{-}C_4H_9)NH][BETI]$	7520	107	49.6	21.3	13.4
7	$[(C_2H_5)_3NH][NTf_2]$	13800	571	270	104	53.9
8	$[(C_2H_5)_3NH][BETI]$	159000	604	256	94.9	50.8
19	$[(n\text{-}C_8H_{17})_3NH][NTf_2]$	0.571	0.329	0.222	0.161	0.235

Correlation of D_{Sr} values with acidities of aqueous phase



Comparison of D_{Sr} for ammonium-based ILs and imidazolium-based ILs



CONCLUSION

1. Over twenty new ammonium-based ionic liquids have been synthesized and characterized.
2. The extraction efficiencies of trialkylammonium-based IL extraction systems using BOBCalixC6 and DCH18C6 have been studied with comparison to the imidazolium-based extraction systems.
3. These new protic extraction systems exhibit the enhanced extraction efficiencies resulted from the increased hydrophilicity of the corresponding IL cations.
4. A strong dependence of the extraction efficiencies on pH has been observed, indicating the possibility for the development of stripping strategies based on pH swing.

ACKNOWLEDGMENT

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