Journal of Chromatography A, xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review article

Recent advances on ionic liquid uses in separation techniques

A. Berthod[a,*], M.J. Ruiz-Ángel[b], S. Carda-Broch[c]

[a] Institut des Sciences Analytiques, Université de Lyon, CNRS, 5 rue de la Doua, 69100, Villeurbanne, France
[b] Departament de Química Analítica, Universitat de València, c/Dr. Moliner 50, 46100, Burjassot, Spain
[c] Departament de Química Física i Analítica, Universitat Jaume I, Avenida Sos Baynat s/n, 12071, Castelló, Spain

ARTICLE INFO

Article history:
Received 12 July 2017
Received in revised form
13 September 2017
Accepted 19 September 2017
Available online xxx

Keywords:
Ionic liquids
Liquid chromatography
Gas chromatography
Deep eutectic solvent
Trace anion detection

ABSTRACT

The molten organic salts with melting point below 100 °C, commonly called ionic liquids (ILs) have found numerous uses in separation sciences due to their exceptional properties as non molecular solvents, namely, a negligible vapor pressure, a high thermal stability, and unique solvating properties due to polarity and their ionic character of molten salts. Other properties, such as viscosity, boiling point, water solubility, and electrochemical window, are adjustable playing with which anion is associated with which cation. This review focuses on recent development of the uses of ILs in separation techniques actualizing our 2008 article (same authors, *J. Chromatogr. A*, 1184 (2008) 6–18) focusing on alkyl methylimidazolium salts. These developments include the use of ILs in nuclear waste reprocessing, highly thermally stable ILs that allowed for the introduction of polar gas chromatography capillary columns able to work at temperature never seen before (passing 300 °C), the use of ILs in liquid chromatography and capillary electrophoresis, and the introduction of tailor-made ILs for mass spectrometry detection of trace anions at the few femtogram level. The recently introduced deep eutectic solvents are not exactly ILs, they are related enough so that their properties and uses in countercurrent chromatography are presented.

1. Introduction

Ionic liquids (ILs) are organic molten salts with melting point lower than 100 °C. If the IL melting point is below room temperature, the liquid is called a room temperature ionic liquid (RTIL) [1]. Since their rediscovery at the end of the last century, these innovative fluids have found uses and applications in all branches of chemistry including organic syntheses, chemical engineering, both focusing on catalysis and solvent IL properties, or preparing new materials, and also, using the versatility and “green” character of ILs, pharmaceutical and environmental science [2].

ILs are made by associating large organic cations with a wide variety of anions. The most common IL cations include: imidazolium, pyridinium, pyrrolidinium and their mono or poly-alkyl derivatives as well as tetraalkyl ammonium or phosphonium and trialkyl sulfonium. Classical IL anions include, for the low metling ILs: bis(trifluoromethylsulfonyl)imide (NTf_2), trifluoromethylsulfate (TfO), dicyanamide ($N(CN)_2$), tetrafluoroborate (BF_4) or hexafluorophosphate (PF_6). Simple anions are also found in less stable ILs or not liquid at room temperature including: chloride, bromide, iodide, nitrate, perchlorate, formate or acetate [1,34]. Other anions can produce ILs as illustrated by the selective alkylmethylimidazolium IL list found in Table 1.

ILs found numerous uses in analytical chemistry and especially in separation techniques as previously described in our 2008 article [3]. This review will focus on the developments observed since 2008 in the use of ILs in separation techniques actualizing our previous text and avoiding repeating or only briefly recalling what was already presented.

2. Selected physicochemical properties of ionic liquids

ILs were dubbed “designer solvents” because they were so versatile that their cation and/or their anion could be adapted to the role that they had to play [4]. Their valuable physicochemical properties include a low melting point (m.p. < 100 °C), very low vapor pressure, high thermal stability, high electrical conductivity, a wide electrochemical window, a low surface tension and an adjustable solvent viscosity and/or polarity and/or hydrophobicity associated with low or high water miscibility [4]. In separation techniques, the important parameters are the IL melting point, viscosity, vapor pressure, thermal stability and solvent properties.

* Corresponding author.
E-mail address: berthod@univ-lyon1.fr (A. Berthod).

http://dx.doi.org/10.1016/j.chroma.2017.09.044
0021-9673/

Table 1
Physicochemical properties of selected methylimidazolium ionic liquids sorted by the cation.[a]

Cation[a]	Anion[b]	formula	m.w. g/mol	m.t.[c] °C	Visc[d] cP 25 °C	Visc[d] cP 50 °C	Density g/mL 25 °C	Decomposition t.[e] °C
mim	Cl	C4H7ClN2	118.6	74	Solid	Solid		
	NO_3	C4H7N3O3	145.1	71	Solid	Solid		
Mmim	Cl	C5H9ClN2	132.6	126	Solid	Solid	1.140	253
Emim	Cl	C6H11ClN2	146.6	89	Solid	Solid	1.110	285
	SCN	C7H11N3S	169.3	−6	29	12	1.117	
	Acetate	C8H14N2O2	170.2	−2	144	39	1.090	221
	NO_3	C6H11N3O3	173.2	39	Solid			
	$N(CN)_2$	C8H11N5	177.2	−18	16	9		275
	Br	C6H11BrN2	191.1	75	Solid	Solid	1.388	311
	BF_4	C6H11BF4N2	198	13	35	18	1.285	447
	Alaninate	C9H17N3O2	199.2	12	260	62		
	$C(CN)_3$	C10H11N5	201.2	−9	15	7		450
	CH_3SO_3	C7H14N2O3S	206.3	25	167	47	1.210	293
	CF_3SO_3	C7H11F3N2O3S	260.2	−14	43	20	1.380	340
	HSO_4	C6H12N2O4S	208.2	19	1600	360	1.470	
	CH_3SO_4	C7H14N2O4S	222.3	−40	79	30		390
	$C2SO_4$	C8H16N2O4S	236.3	−37	98	35	1.235	408
	$C4SO_4$	C10H20N2O4S	264.3	−15	181	56		
	$C6SO_4$	C12H24N2O4S	292.4	−6	320	86		
	$C8SO_4$	C14H28N2O4S	320.5	10	580	140		
	I	C6H11IN2	238.1	78	Solid	Solid		303
	PF_6	C6H11F6N2P	256.1	60	Solid	Solid		380
	$AlCl_4$	C6H11AlCl4N2	280	6.5				
	$TolSO_3$	C13H18N2O3S	282.4	50	Solid	240		
	AsF_6	C6H11AsF6N2	300.1	53	Solid	Solid		416
	NTf_2	C8H11F6N3O4S2	391.3	−17	33	16	1.520	419
	$N(SO_2C_2F_5)_2$	C10H11F10N3O4S2	491.3	−1				423
EMmim	Br	C7H13BrN2	205.1	141	Solid	Solid		322
	NTf_2	C9H13F6N3O4S2	405.3	25	Solid			456
	$N(SO_2C_2F_5)_2$	C11H13F10N3O4S2	505.3	25	Solid			420
Pmim	Cl	C7H13ClN2	160.6	62	Solid	Solid		282
	Br	C7H13BrN2	205.1	28	Solid		1.356	
	BF_4	C7H13BF4N2	212	−17	74	27	1.235	435
	I	C7H13IN2	252.1	17				296
	PF_6	C7H13F6N2P	270.2	38	Solid			435
	NTf_2	C9H13F6N3O4S2	405.3	15	46	19	1.475	452
Bmim	Cl	C8H15ClN2	174.5	41	Solid	150	1.080	154
	SCN	C9H15N3S	197.3	−6	51	19	1.070	
	Acetate	C10H18N2O2	198.3	−1	430	67	1.055	216
	$N(CN)_2$	C10H15N5	205.3	−5	42	19		
	Br	C8H15BrN2	219.1	75	Solid	Solid	1.291	272
	BF_4	C8H15BF4N2	226	−82	108	36	1.212	299
	$C(CN)_3$	C12H15N5	229.3	−20	34	12		
	HSO_4	C8H16N2O4S	236.3	28	Solid			245
	ClO_4	C8H15ClN2O4	238.7	8	180	57		221
	CH_3SO_4	C9H18N2O4S	250.3	−4	94	32	1.213	295
	Trifluoro acetate	C10H15F3N2O2	252.2	0	77	25		
	PF_6	C8H15F6N2P	284.2	11	270	74	1.363	349
	CF_3SO_3	C9H15F3N2O3S	288.3	14	80	31	1.290	340
	Cyclohexyl sulfamate	C14H27N3O3S	317.5	72.5	Solid	Solid		
	$FeCl_4$	C8H15Cl4FeN2	337	−12	41	18		
	$C8SO_4$	C16H32N2O4S	348.5	24	870	152		341
	NTf_2	C10H15F6N3O4S2	419.4	−5	42	19	1.351	332
Isobutylmim	NTf_2	C10H15F6N3O4S2	419.4	−16			1.428	
MMMMmim	NTf_2	C10H15F6N3O4S2	419.4	118	Solid	Solid		370
BMmim	Cl	C9H17ClN2	188.7	93	Solid	Solid		
	BF_4	C9H17BF4N2	240.1	32	Solid	31	$1.182^{40°}$	430
	PF_6	C9H17F6N2P	298.2	38	Solid		$1.338^{40°}$	436
	NTf_2	C11H17F6N3O4S2	433.4	−6	350	34		439
Allylmim	$N(CN)_2$	C9H11N5	189.2	−20	20	10		
Benz mim	Cl	C11H13ClN2	208.7	14	3725	417		278
	CH_3SO_4	C12H16N2O4S	284.3	18	4500	327		
	PF_6	C11H13F6N2P	318.2	130	Solid	Solid		
C5mim	PF_6	C9H17F6N2P	298.2	16	380	97	1.328	
	NTf_2	C11H17F6N3O4S2	433.4	−9	58	22	1.403	
Hmim	$N(CN)_2$	C12H19N5	233.3	1	50	20		
	BF_4	C10H19BF4N2	254.1	−82	200	58	1.149	320
	I	C10H19IN2	294.2	30	Solid	246		
	PF_6	C10H19F6N2P	312.2	−61	480	120	1.295	317
	CF_3SO_3	C11H19F3N2O3S	316.3	25	Solid	47		
	NTf_2	C12H19F6N3O4S2	447.4	−6	70	27	1.372	328